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ELECTRICAL RESISTIVITY DUE TO IMPURITIES
AND DISLOCATIONS IN SIMPLE METALS

by



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A THESIS

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The undersigned certify that they have read,
and recommend to the Faculty of Graduate Studies
for acceptance, a thesis entitled ELECTRICAL
RESISTIVITY DUE TO IMPURITIES AND DISLOCATIONS
IN SIMPLE METALS, submitted by Om Parkash Gupta
in partial fulfilment of the requirements for the
degree of Doctor of Philosophy.

ABSTRACT

Using the pseudopotential formalism, calculations are made for the residual resistivity of alloys, deviations from Matthiessen's rule and the resistivity due to dislocations in metals.

Residual Resistivity of Alloys: It is shown that the failure of Harrison (1966) to obtain a good agreement with experimental residual resistivities is primarily due to the fact that his calculation of the form factors of an impurity ion takes a rather limited account of the effect on them of the change in the surroundings of the ion compared to the case of the ion in the pure metal. Taking a proper account of this effect and on considering a few further improvements (nonlocal screening, effective mass etc.) a satisfactory agreement with experiment is obtained.

Deviations from Matthiessen's Rule: Attention is drawn to an interesting cause of the deviations Δ from Matthiessen's rule which arise from the interference between the scattering due to lattice vibrations of the host atoms and the excess potential due to the impurities. A semiquantitative comparison with experiment based on the impurity form factors introduced above, shows that for simple metals at high temperatures, the deviations

resulting from such an interference, make a significant contribution to Δ .

Resistivity due to Dislocations: Treating the dislocation as a row of weak scatterers with a spherically symmetric potential, an exact solution of the Boltzmann equation in the presence of a set of parallel dislocations is obtained. This is used for making a systematic calculation of the resistivity in the Harrison model of the dislocation. It is also pointed out that the usual method of calculating the resistivity due to random dislocations from the resistivity of parallel dislocations would be violated under certain conditions and an alternative method is explored.

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INTRODUCTION

This thesis is concerned with a study, based on the pseudopotential formalism, of (a) the residual resistivity of alloys and the deviations from Matthiessen's rule, and (b) the resistivity due to dislocations.

The first attempts to explain quantitatively the electrical resistivity phenomenon came after the advent of quantum mechanics, particularly through the work of Bloch, Nordheim, Mott and Bardeen.

The essential step in the estimation of the electrical resistivity is the calculation of $P(\vec{k}, \vec{k}')$, the probability, per unit time, that an electron in a state characterized by the wave vector \vec{k} is scattered to another state of wave vector \vec{k}' . This scattering arises from the aperiodicity of the lattice potential caused by disorders relating to the structure (thermal vibrations, lattice distortions etc.) and/or to the composition (presence of impurities). The forementioned works are based on obtaining $P(\vec{k}, \vec{k}')$ by calculating the perturbing potential, the difference in the potential in the perturbed and the perfect lattice, due to the various mechanisms. This aspect of the subject has been reviewed in many excellent texts [Mott and Jones (1936), Wilson (1953), Ziman (1960)].

In the last decade an alternative approach, known as the effective potential theory, has been developed by Phillips and Kleinman (1959), Austin, Heine and Sham (1962), Harrison (1963), Ziman (1964), and Abarenkov and Heine (1965).

The advantage of this approach is that since the effective potential is weak, one can work directly with the total potential, instead of with the perturbing potential. The scattering can then be written as a product of atom form factors and the structure factor (or the partial structure factors in the case of an alloy). The former depend only on the individual (pseudo-) atoms and the latter only on their arrangement in the crystal. Such a factorization is a consequence of the weak scattering formalism and has been known for a long time in X-ray and neutron scattering theories. Its application to electron scattering and electrical resistivity problems was first made by Krishnan and Bhatia (1945) and Bhatia and Krishnan (1948). The effective potential formalism enables one to calculate the atom form factors and hence the electrical resistivities quantitatively [Ziman (1961), Faber and Ziman (1965) and Harrison (1963, 1966)].

The effective potential theory has been formulated in three different ways. The earliest approach is known as the pseudopotential method which is the one used in this thesis. The other two are the quasi- and the model potentials. The three methods differ from each other only in the calculation of the form factors. The calculation of the properties of metals and alloys proceeds exactly the same way in all the three methods.

The thesis is divided into three parts. Part I deals with the background material. Part II discusses the residual

resistivity of dilute alloys and deviations from Matthiessen's rule. Part III is devoted to the resistivity due to dislocations.

In Chapter 1 we collect together some formulae for calculating the electrical resistivity if $P(\vec{k}, \vec{k}')$ is known. In Chapter 2 we review the pseudopotential technique which forms the basis of our calculations of $P(\vec{k}, \vec{k}')$.

In Chapter 3 we show that the environment of an ion, which changes on alloying, has a much greater effect on the form factors of the ion than had been considered in the calculations of Harrison (1966). On calculating the impurity form factors by taking a proper account of this fact, the agreement with experimental residual resistivities is found to be much better than obtained by Harrison.

In Chapter 4 we point out an interesting cause of the deviation (Δ) from Matthiessen's rule which arises from the interference between the scattering due to lattice vibrations of the host atoms and the excess potential due to the impurities. Such interference terms are missed out in most previous treatments of the problem [Koshino (1960), Taylor (1962, 1964) and by Damon, Mathur and Klemens (1968)] (and references given there) because of the usual practice of adding the probabilities of scattering, rather than the scattering amplitudes, due to the two mechanisms. We shall see that these interference terms play an important part in determining both the qualitative and quantitative behaviour of Δ , particularly at high temperatures.

In Chapter 5 we give a brief survey of the experimental situation and the previous theories of the resistivity due to dislocations. Chapter 6 and 7 give the results of our investigation of this problem.

PART I

THE BACKGROUND MATERIAL

Chapter 1

METHODS OF SOLVING THE BOLTZMANN EQUATION AND THE CALCULATION OF ELECTRICAL RESISTIVITY

§1.1 Elementary solution of the Boltzmann Equation

The standard treatment of electrical resistivity entails the solution of the Boltzmann transport equation, which in the steady state, is given by

$$\left[\frac{\partial f_{\vec{k}}}{\partial t} \right]_{\text{field}} + \left[\frac{\partial f_{\vec{k}}}{\partial t} \right]_{\text{collision}} = 0, \quad (1.1)$$

where $f_{\vec{k}}$ is the distribution function of the electrons i.e.

$\frac{1}{(2\pi)^3} f_{\vec{k}} d\vec{k}$ is the number of electrons of a given spin per unit volume of wave vector space $d\vec{k}$.

In (1.1) the first term arises from the drift of the electrons in the presence of the electric field $\vec{\epsilon}$, and is given by

$$\left[\frac{\partial f_{\vec{k}}}{\partial t} \right]_{\text{field}} = - \frac{e\vec{\epsilon}}{\hbar} \cdot \frac{\partial f_{\vec{k}}}{\partial \vec{k}}. \quad (1.2a)$$

For weak fields this may be approximated to

$$\left[\frac{\partial f_{\vec{k}}}{\partial t} \right]_{\text{field}} \approx - \frac{e\vec{\epsilon}}{\hbar} \cdot \frac{\partial f_{\vec{k}}^0}{\partial \vec{k}}, \quad (1.2b)$$

where $f_{\vec{k}}^0$ is the equilibrium (Fermi-Dirac) distribution function.

The second term in (1.1) represents the change in f due to collisions. If $P(\vec{k}, \vec{k}')$ denotes the probability, per unit time, that an electron in state \vec{k} makes a transition to state \vec{k}' , then $\left[\frac{\partial f_{\vec{k}}}{\partial t} \right]_{\text{coll}}$ is given by *

$$\left[\frac{\partial f_{\vec{k}}}{\partial t} \right]_{\text{coll}} = - \int \{ f_{\vec{k}'} (1 - f_{\vec{k}}) P(\vec{k}, \vec{k}') - f_{\vec{k}} (1 - f_{\vec{k}'}) P(\vec{k}', \vec{k}) \} d\vec{k}'. \quad (1.3)$$

In general, the Boltzmann equation cannot be solved exactly. However if (1) the scattering is elastic i.e., $E_{\vec{k}} = E_{\vec{k}'}$, and hence $P(\vec{k}, \vec{k}') = P(\vec{k}', \vec{k})$, (2) $P(\vec{k}, \vec{k}')$ depends only on $|\vec{k} - \vec{k}'|$, and (3) Fermi surface is spherical, then a simple solution for f can be readily obtained. To see this we first note that for weak fields, f can be taken, quite generally, to be of the form

* Following the normal practice we shall take the crystal volume $\Omega=1$ and omit the factors $\frac{1}{8\pi^3}$ and $\frac{1}{4\pi^3}$ in the \vec{k}' - and \vec{k} -integrations. Note that in the \vec{k} -integration we have a factor 2 arising from the spin multiplicity; it does not appear in the \vec{k}' -integration because scattering takes place only between some spin states.

$$f_{\vec{k}} = f_{\vec{k}}^0 - \left(\frac{e\vec{\epsilon}}{\hbar} \cdot \text{grad}_{\vec{k}} E \right) \frac{\partial f_{\vec{k}}^0}{\partial E_{\vec{k}}} \tau_{\vec{k}}, \quad (1.4)$$

where $\tau_{\vec{k}}$ has the dimensions of time and is, as yet, an unknown function of \vec{k} . Now for elastic scattering (1.3) reduces to

$$\left[\frac{\partial f_{\vec{k}}}{\partial t} \right]_{\text{coll}} = - \int (f_{\vec{k}} - f_{\vec{k}'}) P(\vec{k}, \vec{k}') d\vec{k}', \quad (1.5)$$

and hence substituting (1.4) into (1.5) and using (1.1) and (1.2b), one obtains for $\tau_{\vec{k}}$ the integral equation

$$1 = \int (\tau_{\vec{k}} - \tau_{\vec{k}'}) \frac{\vec{\epsilon} \cdot \text{grad}_{\vec{k}} E}{\vec{\epsilon} \cdot \text{grad}_{\vec{k}'} E} P(\vec{k}, \vec{k}') d\vec{k}'. \quad (1.6)$$

For a spherical Fermi surface (1.6) reduces to

$$1 = \int (\tau_{\vec{k}} - \tau_{\vec{k}'}) \frac{\vec{\epsilon} \cdot \vec{k}'}{\vec{\epsilon} \cdot \vec{k}} P(\vec{k}, \vec{k}') d\vec{k}'. \quad (1.7)$$

If one now takes $P(\vec{k}, \vec{k}') = P(|\vec{k} - \vec{k}'|)$ so that $P(\vec{k}, \vec{k}')$ depends only on the angle θ between the incident and the scattered directions (and not separately on \vec{k} and \vec{k}'), then one obtains for $\tau_{\vec{k}}$ the expression*

$$1/\tau_k = \int (1 - \cos\theta) P(|\vec{k} - \vec{k}'|) d\vec{k}', \quad (1.8)$$

* Note that $P(\vec{k}, \vec{k}')$ is proportional to $\delta(E_{\vec{k}} - E_{\vec{k}'})$ so that the integral in (1.7) is essentially a two dimensional one.

which is independent of the direction of \vec{k} .

Using (1.8) the resistivity may be readily obtained as below.

The current density \vec{J} is given by

$$\vec{J} = e \int \vec{v}_{\vec{k}} f_{\vec{k}} d\vec{k} . \quad (1.9)$$

Substituting (1.4) and restoring the factor $1/4\pi^3$ which had been left understood, one obtains

$$\vec{J} = - \frac{e^2}{4\pi^3 \hbar} \int \tau_k \vec{v}_{\vec{k}} (\vec{\epsilon} \cdot \hat{k}) \frac{\partial f_k^0}{\partial E_k} dE_k dS_k$$

where \hat{k} is a unit vector in the direction of \vec{k} and dS_k is a surface element on the energy surface in k -space with energy E_k . Taking the components of \vec{J} along arbitrarily chosen Cartesian axes, one gets

$$\begin{aligned} J_i &= - \frac{e^2}{4\pi^3 \hbar^2} \int \tau_k \frac{dE_k}{dk} \frac{\partial f_k^0}{\partial E_k} dE_k \int (\vec{\epsilon} \cdot \hat{k}) \hat{k}_i dS_k \\ &= - \frac{e^2 \epsilon_i}{3\pi^2 \hbar^2} \int \tau_k k^2 \frac{dE_k}{dk} \frac{\partial f_k^0}{\partial E_k} dE_k . \end{aligned} \quad (1.10)$$

Remembering that for any smoothly varying function $g(E)$

$$\int g(E) \frac{\partial f^0}{\partial E} dE \approx -g(E_F) \quad (1.11)$$

for $k_B T \ll E_F$, one gets

$$J_i = \frac{e^2 \epsilon_i}{3\pi^2 \hbar^2} \left[\tau_k k^2 \frac{dE_k}{dk} \right]_F . \quad (1.12)$$

Comparing this with the definition of the conductivity tensor

$$J_i = \sum_j \sigma_{ij} \epsilon_j, \quad (1.13)$$

one finds that for this case

$$\sigma_{ij} = \frac{e^2}{3\pi^2 \hbar^2} \left[\tau_k k^2 \frac{dE_k}{dk} \right]_F \quad i=j, \quad (1.14)$$

$$= 0 \quad i \neq j. \quad (1.15)$$

Thus here the conductivity tensor is represented by a single number σ_{ii} which is the same for $i=1,2,3$ and we may write it as σ , the conductivity. Its reciprocal ρ is the resistivity.

Notice that σ in (1.14) is proportional to the square of $\left(\frac{dE_k}{dk}\right)_F$ - the other factor of $\frac{dE_k}{dk}$ arises from τ_k . For metals where the Fermi surface can be assumed to be spherical, it is usually possible also to assume that the E-k relation is parabolic so that for these metals σ is proportional to $(m^*/m)^{-2}$ [or $\rho \propto (m^*/m)^2$], where m^* is the effective mass for the electrons in the metal and m the

free-electron mass.* For this case (1.14) can be written in the convenient form

$$\sigma = \frac{ne^2\tau_{k_F}}{m^*}, \quad (1.16)$$

where n is the density of electrons. Although n appears explicitly in (1.16), it may be noted that, as will be clear from (1.14), the conductivity (and other transport properties) are determined entirely by the electrons at the Fermi surface. The low-lying electrons are, of course, important but only in building up the Fermi level.

* It may be mentioned here that the appearance of $(m^*/m)^2$ in the expression for σ has been a subject of some doubt since the work of Edwards (1962) and Faber (1966) who gave a formalism for calculating σ without using the Boltzmann equation (according to these authors σ should be independent of (m^*/m)); For a recent review on this point see Mott (1967); see also §3.3 of the thesis.

§1.2 Discussion of the General Case and Variational Principle

In the general case when $P(\vec{k}, \vec{k}')$ depends on the directions of \vec{k} and \vec{k}' separately or (and) the Fermi surface is not spherical, $\tau_{\vec{k}}$ would depend on the direction of \vec{k} and the integral equation (1.6) or (1.7) has to be solved for each specific case. An alternative but equivalent method of solving the Boltzmann equation for these cases consists of expanding distribution function in spherical harmonics, which we shall use in Chapter 6 on dislocations. In general, however, one has to resort to approximate methods, in particular, the variational technique which is applicable for both elastic and inelastic scattering.

Before describing this technique, we remark that the conductivity tensor σ_{ij} will now, in general, not be a scalar. However, it follows from Onsager's reciprocity relations that $\sigma_{ij} = \sigma_{ji}$. Now for a symmetrical tensor of rank 2, it is always possible to choose a set of axes, called the principal axes, with respect to which the non-diagonal components of the tensor are zero. With respect to these axes, the non-diagonal components of the resistivity tensor ρ_{ij}

$$\rho_{ij} = \frac{1}{\Delta} (\text{cofactor of } \sigma_{ij})$$

where Δ is the determinant of $|\sigma_{ij}|$, will also be zero.*

Clearly along the principal axes, $\vec{J} \parallel \vec{\epsilon}$ and for such cases the variational expression for the resistivity is given by [see, for example, Ziman (1960)]

$$\rho = \frac{\frac{1}{2k_B T} \int (\phi_{\vec{k}} - \phi_{\vec{k}'})^2 Q(\vec{k}, \vec{k}') d\vec{k} d\vec{k}'}{\left| \text{ev}_{\vec{k}} \phi_{\vec{k}} \frac{\partial f_{\vec{k}}^0}{\partial E_{\vec{k}}} d\vec{k} \right|^2}, \quad (1.17)$$

where $Q(\vec{k}, \vec{k}')$ is defined by

$$Q(\vec{k}, \vec{k}') [=Q(\vec{k}', \vec{k})] = f_{\vec{k}}^0 (1 - f_{\vec{k}'}^0) P(\vec{k}, \vec{k}'), \quad (1.18)$$

and $\phi_{\vec{k}}$ is a trial function connecting the perturbed distribution function $f_{\vec{k}}$ with the equilibrium distribution function $f_{\vec{k}}^0$ by the relation

$$f_{\vec{k}} = f_{\vec{k}}^0 - \phi_{\vec{k}} \frac{\partial f_{\vec{k}}^0}{\partial E_{\vec{k}}}. \quad (1.19)$$

The variational principle states that $\phi_{\vec{k}}$ must be chosen to make ρ of (1.17) a minimum.

Thus the problem of finding ρ boils down to (i) selecting a trial function with adjustable parameter/s,

* For cubic symmetry, the three principal (diagonal) components of σ_{ij} or ρ_{ij} are equal and σ and ρ are scalar.

(ii) determining the parameters by minimizing (1.17), and
 (iii) substituting the, now known, parameters back into
 (1.17) to get ρ . Reasonable results can often be obtained
 by using the simplest trial function

$$\phi_{\vec{k}} = \alpha \vec{k} \cdot \hat{\epsilon}, \quad (1.20)$$

where $\hat{\epsilon}$ is a unit vector in the direction of the electric
 field and α is a constant [the value of which does not
 matter since it cancels out from (1.17)].

Chapter 2

PSEUDOPOTENTIALS IN METALS AND THE CONCEPT OF WEAKLY SCATTERING NEUTRAL PSEUDO-ATOMS

One of the most interesting things about the valence electrons in metals is the extent to which their observed properties can be explained in terms of models where either the ions are ignored or their role vastly simplified, except for maintaining charge neutrality. Another interesting thing is that it is not readily apparent why such models should work at all: The nearly free electron approximation, for example, requires the atomic potential to be weak compared with the bandwidth, and this certainly is not the case. It was pointed out by Phillips and Kleinmann (1959) (to be abbreviated PK) that the reason for this is that in the region of the ion core where the potential is the deepest, there is an almost complete cancellation between the large negative potential energy and the large positive kinetic energy associated with the rapid oscillations of the wave function at the core. The observable effects are produced by a weak net potential which has come to be called the pseudopotential. Not only did this provide an immediate understanding of the nearly-free behaviour of the electrons, it set the stage for the development of the theory of metals from an entirely new point of view.

Previously, whenever one wanted to calculate the field due to some arrangement of ions - for example, in

the neighbourhood of a dislocation in an otherwise perfect lattice - one was confronted with the problem of allowing for the redistribution of charge in the electron gas and for the field that this produces. The construction of a self-consistent field in such circumstances was a major difficulty. However, if the effective interaction between the ions and the electrons is weak we can use the approximation of linear screening according to which the perturbations of the electron gas due to different ions can be added independently provided the screening cloud is not too large a fraction of the total electron density. This now leads to the result that in any arrangement of the ions, the ion and its screening charge may be considered as a single entity. The entity is electrically neutral and is called a pseudo-atom. After we have built up, say, a dislocation out of these neutral pseudo-atoms, there can be no further charge shift; all the conduction electrons have been automatically accounted for and their potential is already contained in the potential of the pseudo-atoms. Furthermore, the field due to each pseudo-atom being the (linearly) screened pseudopotential of the real ion, the scattering due to each pseudo-atom is weak and in any problem the information relating to the arrangement of the ions enters only through a structure factor (or structure factors if we are dealing with an alloy). Thus, we can hope to apply the theory, as has indeed been done, to a study of the general proper-

ties rather than simply the properties of perfect, undistorted crystals.

It should be emphasized that the concept of the weakly scattering pseudo-atom, despite its simplicity and apparent naivety, is not a phenomenological model. It is based upon the true physical system and is almost as precise in detail as the best calculations that have been made. However, it may be mentioned that the pseudopotential formalism is based on the small-core approximation, i.e. overlap of core wave functions of adjacent ions is negligible*. Because of this the method can be applied only to the alkali and poly valent metals, or simple metals as they are called. Its application to noble metals is questionable and to transition metals, it is quite inappropriate.

In this chapter we wish to describe the pseudo-potential formalism, the concept of the pseudo-atom and the calculation of the scattering from a single pseudo-atom. Since the first two points relate to the general properties of pseudopotentials, the discussion of these points would apply to pure metals as well as alloys.

* This remark equally well to the other two formulations of the effective potential theory.

However, the explicit calculation of the scattering from a pseudo-atom will here be discussed only for a pure metal, the modification of the scattering on alloying to be taken up later.

§2.1 The Pseudopotential Method - Formal Work

§2.1.1 The P-K Formulation

The formulation of Phillips and Kleinmann employs the orthogonalized plane wave (OPW) method which is based on expanding the (true) wave function $\psi_{\vec{k}}$ in terms of plane waves orthogonalized to the core states. Thus

$$\psi_{\vec{k}} = \sum_{\vec{q}} a_{\vec{q}}(\vec{k}) \chi_{\vec{k}+\vec{q}}, \quad (2.1)$$

where the orthogonalized plane waves $\chi_{\vec{k}}$ are given by

$$\begin{aligned} \chi_{\vec{k}} &= |\vec{k}\rangle - \sum_{\alpha} |\alpha\rangle \langle \alpha | \vec{k} \rangle \\ &\equiv (1 - P) |\vec{k}\rangle, \end{aligned} \quad (2.2)$$

the projection operator P being given by

$$P = \sum_{\alpha} |\alpha\rangle \langle \alpha|. \quad (2.3)$$

Here $|\vec{k}\rangle$ are plane waves normalized to unity over the crystal volume Ω , $|\alpha\rangle$ are the core states, the term $P|\vec{k}\rangle$ in $\chi_{\vec{k}}$ is for making the latter orthogonal to $|\alpha\rangle$.

Now $\psi_{\vec{k}}$ satisfies the equation

$$(T + V) \psi_{\vec{k}} = E_{\vec{k}} \psi_{\vec{k}} \quad (2.4)$$

where T is the kinetic energy, $-\hbar^2 \nabla^2 / 2m$, V is the true potential and $E_{\vec{k}}$ the eigenvalue of the Hamiltonian for the eigenfunction $\psi_{\vec{k}}$. On substituting (2.1) and (2.2) in (2.4), using $(T+V)|\alpha\rangle = E_{\alpha}|\alpha\rangle$ where E_{α} is the energy of the core state $|\alpha\rangle$, and rearranging we get

$$(T + W) \phi_{\vec{k}} = E_{\vec{k}} \phi_{\vec{k}} \quad (2.5)$$

where

$$\phi_{\vec{k}} = \sum_{\vec{q}} a_{\vec{q}}(\vec{k}) |\vec{k} + \vec{q}\rangle \quad (2.6)$$

and

$$W\phi_{\vec{k}} = V\phi_{\vec{k}} + \sum_{\alpha} (E_{\vec{k}} - E_{\alpha}) |\alpha\rangle \langle \alpha | \phi_{\vec{k}} \rangle \quad (2.7)$$

Thus the true wave function $\psi_{\vec{k}}$ and the true potential V may be replaced by $\phi_{\vec{k}}$ and W respectively without affecting the energy eigenvalue. $\phi_{\vec{k}}$ is called the pseudo wave function and W the pseudopotential.

We notice the following points:-

(a) From (2.1), (2.2) and (2.6) we get

$$\psi_{\vec{k}} = \phi_{\vec{k}} - \sum_{\alpha} |\alpha\rangle \langle \alpha | \phi_{\vec{k}} \rangle \quad (2.8)$$

so that $\phi_{\vec{k}}$ and $\psi_{\vec{k}}$ are the same outside the region of the core. Using this and (2.5) it can be proved (Austin, Heine

and Sham (1962)) that the equivalence of $(\psi_{\vec{k}}, V)$ problem to the $(\phi_{\vec{k}}, W)$ problem is carried over to the determination of the scattering probability.

(b) The second term in (2.7) is positive. For this reason it is called the repulsive potential and has the effect of largely cancelling V in the core region so that we can use perturbation theory to calculate the scattering and the energy of the eigenstates. Experience shows that for scattering which is what concerns us in this thesis, the results obtained by the lowest order perturbation theory are reasonably accurate.

(c) The repulsive part W^R of W is an integral operator or a nonlocal potential:

$$W^R \phi(\vec{r}) = \int W^R(\vec{r}, \vec{r}') \phi(\vec{r}') d\vec{r}'$$

$$W^R(\vec{r}, \vec{r}') = \sum_{\alpha} (E_{\vec{k}} - E_{\alpha}) \psi_{\alpha}^*(\vec{r}') \psi_{\alpha}(\vec{r})$$

where ψ_{α} is the wave function for the core state $|\alpha\rangle$. Because of this nonlocal character of W^R , its matrix-elements between two states $|\vec{k}\rangle$ and $|\vec{k}+\vec{q}\rangle$ will depend on both \vec{k} and \vec{q} , rather than on \vec{q} alone. Thus we have lost some of the simplicity of the original problem where $V(\vec{r})$ is a local potential. However, the nonlocal nature of W^R only causes some calculational complexity and no fundamental difficulty.

§2.1.2 The Nonuniqueness of PK pseudo wave function and the AHS Theorem

It was pointed out by Cohen and Heine (1961) that the PK pseudopotential does not generate a unique pseudo wave function. $\phi_{\vec{k}}$ is arbitrary to the extent of the addition of a linear combination of the core states. If one adds $\sum_{\alpha} a_{\alpha} |\alpha\rangle$ to $\phi_{\vec{k}}$, where a_{α} is arbitrary, it will remain a solution of (2.5) with the same eigenvalue. Further, one notes from (2.5) that the true wave function also remains unchanged as the addition to the first term is neutralized by a subtraction in the orthogonalization term.

The reason for this nonuniqueness lies in the OPW's $\chi_{\vec{k}}$ being overcomplete, hence nonorthogonal. The plane waves $|\vec{k}\rangle$ are complete and independent, but the effect of orthogonalization is to introduce linear relations among the $\chi_{\vec{k}}$.

The arbitrariness in $\phi_{\vec{k}}$, allows us to impose a constraint on it. This will affect W^R and hence W . Thus depending upon the type of the constraint applied, we will get various forms for W .

It was shown by Austin, Heine and Sham (1962) that the arbitrariness of W is more deep-rooted. In general, the pseudopotential may not be connected with the OPW's at all. They proved that the most general pseudopotential is given by

$$W\phi_{\vec{k}} = V(\vec{r})\phi_{\vec{k}}(\vec{r}) + \sum_{\alpha} \psi_{\alpha}(\vec{r})(f(\vec{r}',\alpha),\phi_{\vec{k}}(\vec{r}')) , \quad (2.9)$$

where $f(\vec{r}',\alpha)$ is an arbitrary function of position and core index α . This result is known as the AHS theorem. In writing (2.9) we have used the inner-product notation

$$(u(\vec{r}), v(\vec{r})) = \int u^*(\vec{r})v(\vec{r})d\vec{r} . \quad (2.10)$$

The relation between the true wave function and the pseudo wave function in the AHS formalism may be deduced from (2.9) and (2.5) making use of the orthogonality of $\psi_{\vec{k}}$ and ψ_{α} . It is given by

$$\phi_{\vec{k}} = \psi_{\vec{k}} + \sum_{\alpha} b_{\alpha} \psi_{\alpha} , \quad (2.11)$$

where b_{α} is determined from the set of equations

$$b_{\alpha}(\vec{k}) (E_{\vec{k}} - E_{\alpha}) = \sum_{\eta} f(\eta,\alpha) a_{\eta}(\vec{k}) \langle \alpha | \eta \rangle , \quad (2.12)$$

where $|\eta\rangle$'s are a complete set of orthonormal states (which may be chosen as plane waves if necessary) and $a_{\eta}(k)$ and $f(\eta,\alpha)$ are defined by the expansions

$$\phi_{\vec{k}} = \sum_{\eta} a_{\eta}(\vec{k}) |\eta\rangle \quad (2.13)$$

$$f(\vec{r},\alpha) = \sum_{\eta} f^*(\eta,\alpha) \langle \eta | \alpha \rangle |\eta\rangle . \quad (2.14)$$

Before we can obtain $b_{\alpha}(\vec{k})$ from (2.12) we will naturally have to eliminate $a_{\eta}(\vec{k})$ using (2.11) and (2.13).

The detailed evaluation of b_α is of no interest to us but we may note that when $f(\eta, \alpha)$ is independent of η and $f(\alpha) = (E_{\vec{k}} - E_\alpha)$, as is the case for the PK pseudopotential, $b_\alpha = \langle \alpha | \phi_{\vec{k}} \rangle$, which is what we obtained earlier in (2.8). It may be noted that this does not imply any particular value of b_α . It really expresses only the orthogonality of $\psi_{\vec{k}}$ and ψ_α and leaves b_α arbitrary, as discussed in the beginning of §2.1.2.

§2.1.3 The Selection of a Pseudopotential

The nonuniqueness of the pseudopotential, discussed in §2.1.2, not only does not give rise to any inconsistency in principle, in practice also it is not entirely a limitation. On the contrary it can be very helpful because it allows us to choose our pseudopotential and by making a judicious choice, one may hope to be able to use simple computational techniques for estimating the observed properties.

Cohen and Heine (1961) suggested that we choose a pseudopotential which leads to a pseudo wave function with the most rapidly convergent plane wave expansion. Such a pseudo wave function might be replaced without much error by a single plane wave - beyond doubt the most convenient representation of ϕ . Cohen and Heine further noted that if we require our pseudopotential to give the smoothest possible pseudo wave function, we might just

get the ϕ we are looking for: it is reasonable to expect that the smoothest ϕ will have an optimum convergence of its expansion in plane waves.

Noting that the criterion of smoothness is equivalent to minimizing

$$\int |\nabla \phi|^2 d\vec{r} / \int |\phi|^2 d\vec{r} \quad (2.15)$$

Cohen and Heine found (see also Harrison (1966) §8.1) that the corresponding W is given by

$$W\phi_{\vec{k}} = (1 - P) V\phi_{\vec{k}} + \frac{(\phi_{\vec{k}}, W\phi_{\vec{k}})}{(\phi_{\vec{k}}, \phi_{\vec{k}})} P\phi_{\vec{k}} . \quad (2.16)$$

(2.16) is not a convenient expression for W because if it is solved explicitly for W , one gets a nonlinear W ; hence (2.16) is not of AHS form. Cohen and Heine suggested that as an approximation, the second term on the R.H.S. of (2.16) (which gives rise to the nonlinearity) be dropped. It was noticed by Austin (see AHS) that this is not an approximation at all, but is still a valid form for W satisfying (2.5). This pseudopotential is called the Austin pseudopotential.

Harrison proceeding somewhat differently about the second term in (2.16) obtained the so-called Harrison pseudopotential. He replaced it by a linear term such that the resulting pseudopotential is equivalent to the pseudopotential in (2.16) up to the second order pertur-

bation theory. This leads to a pseudopotential given by

$$W = V + \sum_{\alpha} |\alpha\rangle\langle\alpha| \left(-\hbar^2 \nabla^2 / 2m + \langle \vec{k} | W | \vec{k} \rangle - E_{\alpha} \right) .$$

Operating it on the zero order state $|\vec{k}\rangle$

$$W|\vec{k}\rangle = V|\vec{k}\rangle + \sum_{\alpha} |\alpha\rangle \left(\hbar^2 k^2 / 2m + \langle \vec{k} | W | \vec{k} \rangle - E_{\alpha} \right) \langle \alpha | \vec{k} \rangle . \quad (2.17)$$

On eliminating $\langle \vec{k} | W | \vec{k} \rangle$ from the right hand side we obtain for the matrix element of W between two plane waves

$$\begin{aligned} & \langle \vec{k} + \vec{q} | W | \vec{k} \rangle \\ &= \langle \vec{k} + \vec{q} | V | \vec{k} \rangle + \sum_{\alpha} \left(\hbar^2 k^2 / 2m + \langle \vec{k} | V | \vec{k} \rangle - E_{\alpha} \right) \langle \vec{k} + \vec{q} | \alpha \rangle \langle \alpha | \vec{k} \rangle \\ &+ \sum_{\alpha} \left(\hbar^2 k^2 / 2m + \langle \vec{k} | V | \vec{k} \rangle - E_{\alpha} \right) \langle \vec{k} | \alpha \rangle \langle \alpha | \vec{k} \rangle \frac{\langle \vec{k} + \vec{q} | P | \vec{k} \rangle}{1 - \langle \vec{k} | P | \vec{k} \rangle} . \end{aligned} \quad (2.18)$$

The smoothness criterion given by Cohen and Heine has been questioned by Abarenkov and Heine (1965) and by Pendry (1968). The issue raised by Abarenkov and Heine is whether we should prefer the smoothest wave function or the smoothest pseudopotential. They suggested the use of a criterion which is a compromise between the two but they found that the calculations became very heavy. Pendry (1968) has suggested that a more useful pseudopotential may be obtained by requiring the pseudopotential to lead to the most rapid

convergence of the Born series. The usefulness of this procedure has still to be demonstrated.

§2.2 Pseudopotential and the Use of Perturbation Theory

In §2.1 we found that the general pseudopotential

$$W\phi_{\vec{k}} = V(\vec{r})\phi_{\vec{k}}(\vec{r}) + \sum_{\alpha} \psi_{\alpha}(\vec{r})(f(\vec{r}, \alpha), \phi_{\vec{k}}(\vec{r})) ,$$

with $\phi_{\vec{k}}$ normalized according to

$$\phi_{\vec{k}} = \psi_{\vec{k}} + \sum_{\alpha} (\psi_{\alpha}, \phi_{\vec{k}}) \psi_{\alpha}$$

reproduces the true valence energies and the true scattering. Now, if we were to attempt an exact solution, we may not find the (ϕ, W) -problem to be much simpler than the original problem of ψ and V . However, the value of the pseudopotential transformation lies in that in the transformed problem, with a suitable choice of W , we can expect to obtain a reasonably good estimate of the exact results for most problems by the use of the perturbation theory. It is this feature which enables one to explore a vast array of the properties of metals, rather than just the energy-band calculations.

The perturbation theory is essentially used in two places: (1), to obtain the screening of the bare pseudopotential and (2), to calculate the scattering from the

screened pseudopotential. In both of these we shall restrict ourselves to the lowest order of perturbation.

§2.3 Separation of the Pseudopotential and the Concept of Pseudo-atoms

So far we have been talking of the total pseudopotential, the pseudopotential due to all the ions and the conduction electrons. But there is an extremely important feature, known as the separation of the pseudopotential without which the formalism would have been of little practical use. This consists in expressing the total pseudopotential as a sum of the potentials centred around individual ionic sites. The potential associated with each site includes the effect of the ion and the screening charge and is ascribed to a neutral entity called a pseudo-atom. The separation of the pseudopotential is achieved in two steps - the separation of the bare pseudopotential and that of the potential due to screening. The former is based on the small core approximation and the latter, on the approximation of linear screening (i.e. on the approximation of estimating the screening by the first order of perturbation). Now we shall briefly describe these two steps.

§2.3.1 Separation of the Bare Pseudopotential

In its most general form the bare pseudopotential is given by

$$W^b |\vec{k}\rangle = V^b |\vec{k}\rangle + \sum_{\alpha} f(\vec{k}, \alpha) |\alpha\rangle \langle \alpha | \vec{k}\rangle \quad , \quad (2.19)$$

where $|\vec{k}\rangle$ is an arbitrary plane wave with vector \vec{k} and the superscript b stands for bare.

First let us show the separability of W^b for a pure metal. The discussion will be found to apply to an alloy with minor modifications, which will be pointed out at the end of §2.3.1.

If the core states are sufficiently localized for the cores of the adjacent ions not to overlap, we can write V^b in a pure metal as

$$V^b(\vec{r}) = \sum_j v^b(\vec{r} - \vec{r}_j) \quad , \quad (2.20)$$

where $v^b(\vec{r} - \vec{r}_j)$ is the bare potential due to an ion seated at \vec{r}_j . The assumption of no overlap of the cores also gives

$$|\alpha\rangle = \psi_t(\vec{r} - \vec{r}_j) \quad , \quad (2.21)$$

where the index α has been separated into the pair of indices j and t ; j as before labels the ions and t denotes the energy and angular-momentum numbers for the core states of the ion. If, now, $f(\vec{k}, \alpha)$ depends on α only through t , we can write

$$W^b |\vec{k}\rangle = \sum_j w^b(\vec{r} - \vec{r}_j) |\vec{k}\rangle \quad , \quad (2.22)$$

with w^b given by

$$\begin{aligned}
w^b(\vec{r} - \vec{r}_j) |\vec{k}\rangle &= v^b(\vec{r} - \vec{r}_j) e^{i\vec{k} \cdot \vec{r}} / \Omega^{\frac{1}{2}} \\
&+ \sum_t f(\vec{k}, t) \psi_t(\vec{r} - \vec{r}_j) \int \psi_t^*(\vec{r}' - \vec{r}_j) (e^{i\vec{k} \cdot \vec{r}'} / \Omega^{\frac{1}{2}}) d\vec{r}' . \quad (2.23)
\end{aligned}$$

(2.22) and (2.23) represent the separation of the total bare pseudopotential into pseudopotentials associated with individual ions.

Now let us examine the reduction of $f(\vec{k}, \alpha)$ into $f(\vec{k}, t)$. Actually, because of the arbitrariness of $f(\vec{k}, \alpha)$ we could always choose for it the form $f(\vec{k}, t)$. But in view of the criterion of the smoothness of the wave function we need to look into this question more closely.

The assumption of no overlap of the cores leads to (2.21) which expresses the fact that the core states are localized at particular ions. Thus E_α must be equal to E_{t_j} . Since, if the boundary effects are neglected, all the sites in a pure metal are equivalent, E_{t_j} must be independent of j . So we have

$$E_\alpha = E_{t_j} = E_t . \quad (2.24)$$

(2.21) and (2.24) immediately give that within the small core approximation $f(\vec{k}, \alpha)$ reduces to $f(\vec{k}, t)$.

It may be pointed out that the small core approximation is important not only in achieving the separation of w^b , but also in estimating E_t and ψ_t . For a sufficiently localized core, we may neglect the variation over the core

of the potentials due to the conduction electrons and the adjacent ions. It follows that the core wave functions are the same as in an isolated ion though the energies of the core states will be different. The difference between the energy of a core state in a metal and the energy of the same state for an isolated ion can be calculated by the Wigner Seitz approximation. Therefore if we know the wave functions and the energies for an isolated ion (which are usually obtained by Hartree-Fock calculations), we can determine ψ_t and E_t in a metal.

It is clear that the separability of W^b will be carried over to the alloys also, since the only modification we will have to make is change v^b , w^b and t to v_j^b , w_j^b and t_j respectively. It may be noted that within the Wigner Seitz approximation E_{t_j} depends upon j only through the specie of the ion occupying the site j and as a result of the small-core approximation, the same clearly applies to ψ_{t_j} . Therefore for a given ion, not only v^b but the whole of w^b is independent of the location of the ion in the crystal.

§2.3.2 Linear Screening and Separation of the Potential due to Screening

Now we shall consider the linear screening of the bare potential W^b . Here we shall directly deal with the

alloys (rather than first doing for the pure metal and then generalizing, as we did in §2.3.1) because here the alloys do not lead to any extra complication.

We shall use the self-consistent approach followed by Bardeen (1937), reformulated in terms of a dielectric function by Lindhard (1954). It has been shown by Ehrenreich and Cohen (1959) that the method is equivalent in many respects to the many-body treatment using the random phase approximation.

In the absence of the ionic potential the density of conduction electrons will be uniform and their wave functions will be plane waves. In the linear approximation, the evaluation of the deviation from the uniform distribution is based on the use of the zero order wave functions corrected to the first order for the effect of the ions. For an electron of wave number \vec{k} , this wave function is

$$\phi_{\vec{k}} = |\vec{k}\rangle + \sum'_{\vec{q}} a_{\vec{q}}(\vec{k}) |\vec{k} + \vec{q}\rangle, \quad (2.25)$$

where the prime over the summation sign indicates the exclusion of $q=0$ and $a_{\vec{q}}(\vec{k})$ is given by the usual first order expression

$$a_{\vec{q}}(\vec{k}) = \frac{\langle \vec{k} + \vec{q} | W | \vec{k} \rangle}{E_{\vec{k}}^0 - E_{\vec{k} + \vec{q}}^0} = \frac{\langle \vec{k} + \vec{q} | W | \vec{k} \rangle}{(\hbar^2/2m)(k^2 - |\vec{k} + \vec{q}|^2)}. \quad (2.26)$$

The electron density corresponding to $\phi_{\vec{k}}$ is given by

$$\phi_{\vec{k}}^* \phi_{\vec{k}} = (1/\Omega) [1 + \sum_{\vec{q}} a_{\vec{q}}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} + a_{\vec{q}}^*(\vec{k}) e^{-i\vec{k} \cdot \vec{r}}]. \quad (2.27)$$

Thus the deviation from the uniform distribution associated with an electron of wave number \vec{k} is

$$(1/\Omega) \sum_{\vec{q}} a_{\vec{q}}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} + a_{\vec{q}}^*(\vec{k}) e^{-i\vec{q} \cdot \vec{r}}, \quad (2.28)$$

which we rewrite as

$$(1/\Omega) \sum_{\vec{q}} [a_{\vec{q}}(\vec{k}) + a_{-\vec{q}}^*(\vec{k})] e^{i\vec{q} \cdot \vec{r}}. \quad (2.29)$$

Summing it up over all the occupied states, we find that $N(\vec{r})$, the total deviation from the uniform density, is given by

$$N(\vec{r}) = \sum_{\vec{q}} N(\vec{q}) e^{i\vec{q} \cdot \vec{r}}, \quad (2.30)$$

where

$$\begin{aligned} N(\vec{q}) &= \frac{1}{4\pi^3} \int d\vec{k} [a_{\vec{q}}(\vec{k}) + a_{-\vec{q}}^*(\vec{k})] \\ &= \frac{1}{2\pi^3} \int \frac{d\vec{k} \langle \vec{k} + \vec{q} | W | \vec{k} \rangle}{(\hbar^2/2m)(k^2 - |\vec{k} + \vec{q}|)^2}. \end{aligned} \quad (2.31)$$

Note that the screening charge density depends upon W (not just on W^b), which requires the knowledge of the screening charge itself. So we have to solve the problem self-consistently.

We note that W is given by

$$W = W^b + W^s, \quad (2.32)$$

where W^S is the contribution due to screening. Further, $W^S(\vec{r})$ is related to $N(\vec{r})$ by the Poisson's equation

$$\nabla^2 W^S(\vec{r}) = -4\pi e^2 N(\vec{r}) ,$$

so that $W^S(\vec{q})$, the Fourier transform of $W^S(\vec{r})$, is given by

$$W^S(\vec{q}) = \frac{4\pi e^2}{q^2} N(\vec{q}) . \quad (2.33)$$

Substituting (2.32) and (2.33) in (2.31) and noting that $W^S(\vec{q})$ is independent of \vec{k} , we get

$$\frac{q^2 W^S(\vec{q})}{4\pi e^2} = \frac{1}{2\pi^3} \int \frac{d\vec{k} \langle \vec{k} + \vec{q} | W^b | \vec{k} \rangle}{(\hbar^2/2m)(k^2 - |\vec{k} + \vec{q}|^2)} - \frac{q^2 W^S(\vec{q})}{4\pi e^2} [\epsilon(q) - 1] , \quad (2.34)$$

where $\epsilon(q)$ is called the dielectric function and is given by

$$\epsilon(q) = 1 + \frac{2me^2 k_F}{\pi q^2 \hbar^2} \left[1 + \frac{4k_F^2 - q^2}{8qk_F} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right] . \quad (2.35)$$

Rearranging (2.34), we get

$$W^S(\vec{q}) = \frac{2e^2}{\pi^2 q^2 \epsilon(q)} \int \frac{d\vec{k} \langle \vec{k} + \vec{q} | W^b | \vec{k} \rangle}{(\hbar^2/2m)(k^2 - |\vec{k} + \vec{q}|^2)} . \quad (2.36)$$

Since W^b has earlier been shown to be separable, we have

$$\langle \vec{k} + \vec{q} | W^b | \vec{k} \rangle = \sum_j \langle \vec{k} + \vec{q} | W_j^b | \vec{k} \rangle e^{-i\vec{q} \cdot \vec{r}_j} , \quad (2.37)$$

so that

$$W^S(\vec{q}) = \sum_j w_j^S(\vec{q}) e^{-i\vec{q} \cdot \vec{r}_j} , \quad (2.38)$$

with

$$w_j^S(\vec{q}) = \frac{2e^2}{\pi^2 q^2 \epsilon(q)} \int \frac{d\vec{k} \langle \vec{k} + \vec{q} | w_j^b | \vec{k} \rangle}{(\hbar^2/2m)(k^2 - |\vec{k} + \vec{q}|^2)} . \quad (2.39)$$

(2.38) immediately gives

$$W^S(\vec{r}) = \sum_j w_j^S(\vec{r} - \vec{r}_j) , \quad (2.40)$$

where

$$w_j^S(\vec{r}) = \sum_{\vec{q}} w_j^S(\vec{q}) e^{i\vec{q} \cdot \vec{r}} . \quad (2.41)$$

(2.40) is the result we had sought to establish.

We can carry the argument a bit further. From (2.38) and (2.33) we can write

$$N(\vec{q}) = \sum_j n_j(\vec{q}) e^{-i\vec{q} \cdot \vec{r}_j} , \quad (2.42)$$

where $n_j(\vec{q})$ is related to $w_j^S(\vec{q})$ in the same manner as $N(\vec{q})$ to $W^S(\vec{q})$. From Fourier inversion of (2.42) we get

$$N(\vec{r}) = \sum_j n_j(\vec{r} - \vec{r}_j) , \quad (2.43)$$

with

$$n_j(\vec{r}) = \sum_{\vec{q}} n_j(\vec{q}) e^{i\vec{q} \cdot \vec{r}_j} . \quad (2.44)$$

Thus we have shown that if the bare pseudopotential is separable, the use of linear screening permits us to

divide the total screening charge into distributions of charge associated with the ion sites. The ion and the screening charge may now be regarded as a single entity giving rise to a potential w given by

$$w = w^b + w^s \quad . \quad (2.45)$$

Since the screening charge equals the charge it screens, this entity must be neutral and is called a pseudo-atom.

In the above discussion we have omitted two important points.

First of all we note that we have taken the zero order energy of the states of wave vector \vec{k} and $|\vec{k}+\vec{q}\rangle$ to be $\hbar^2 k^2/2m$ and $\hbar^2 |\vec{k}+\vec{q}|^2/2m$ respectively. Evidently, the free electron mass m must be replaced by an effective mass m^* .

Secondly, we notice that we have neglected the effect of exchange[†] on the screening charge. It has been shown by Sham (1965) that this effect can be included by multiplying the right hand side of (2.35) and (2.39) by $[1-f(q)]$, and by changing $\epsilon(q)$ to $\epsilon^*(q)$ given by

$$\epsilon^*(q) = 1 + \frac{2me^2 k_F^2}{\pi^2 q^2 \hbar^2} [1-f(q)] \left[1 + \frac{4k_F^2 - q^2}{8qk_F} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right], \quad (2.46)$$

with

$$f(q) = \frac{q^2}{2(q^2 + k_F^2 + k_S^2)} \quad , \quad (2.47)$$

[†]The effect of correlation is not significant [Harrison (1966), p. 323]]

where k_s^{-2} is half the square of the Thomas Fermi screening length wherefore

$$\begin{aligned} k_s^2 &= \frac{1}{2} \cdot 4\pi e^2 \frac{mk_F}{\pi^2 \hbar^2} \\ &= \frac{2k_F}{\pi} \frac{me^2}{\hbar} \quad . \end{aligned} \quad (2.48)$$

It is obvious that while both of these points are important for an explicit calculation of the screening, they do not affect our conclusion regarding the separability of the pseudopotential.

§2.4 First Order Estimate of the Scattering from the Screened Pseudopotential in terms of the Form Factors of Individual Pseudo-atoms

In the first order of perturbation, the probability of scattering from a state with vector \vec{k} to another with wave vector $\vec{k}+\vec{q}$ is determined by the matrix element of W between the zero order states $|\vec{k}\rangle$ and $|\vec{k}+\vec{q}\rangle$. As a result of the separability of W , this matrix element can be written as

$$\langle \vec{k}+\vec{q} | W | \vec{k} \rangle = \sum_j \langle \vec{k}+\vec{q} | w_j | \vec{k} \rangle e^{-i\vec{q} \cdot \vec{r}_j} \quad . \quad (2.49)$$

By defining plane wave states $|\vec{k}\rangle$ and $|\vec{k}+\vec{q}\rangle$ which are the same as $|\vec{k}\rangle$ and $|\vec{k}+\vec{q}\rangle$ respectively except that the former are normalized to unity over Ω_0 , the volume per ion, we

can rewrite (2.49) as

$$\langle \vec{k} + \vec{q} | W | \vec{k} \rangle = (1/N) \sum_j (\vec{k} + \vec{q} | w_j | \vec{k}) e^{-i\vec{q} \cdot \vec{r}_j} , \quad (2.50)$$

where N is the total number of ions in the crystal. The matrix elements $(\vec{k} + \vec{q} | w_j | \vec{k})$ are called the form factors of the pseudo-atom at the site j . The calculation of these form factors is of interest because they can be used to deduce a host of atomic and electronic properties of metals and alloys. That they are related to the transport properties is evident from (2.50). Their relationship with other properties like crystal structure, elastic constants etc. may be looked up in Harrison (1966), Chap. 6.

For a pure metal, w_j is the same for all j and (2.50) takes a particularly convenient form

$$\langle \vec{k} + \vec{q} | W | \vec{k} \rangle = (\vec{k} + \vec{q} | w | \vec{k}) S(\vec{q}) , \quad (2.51)$$

where

$$S(\vec{q}) = (1/N) \sum_j e^{-i\vec{q} \cdot \vec{r}_j} . \quad (2.52)$$

In (2.51) we have a factorization of $\langle \vec{k} + \vec{q} | W | \vec{k} \rangle$, which in our first order treatment represents the scattering amplitude, into a factor $(\vec{k} + \vec{q} | w | \vec{k})$ which depends only on the properties of the atoms and another factor $S(\vec{q})$, called the structure factor, which depends only on the arrangement of the atoms. Such a factorization of the

scattering amplitude is a direct consequence of the use of the first order theory which is equivalent to the assumption of the Born approximation. Below it will be seen that the result is carried over to the more general case of the weak scattering approximation.

It may be pointed out that the relation (2.49) which we obtained by the use of first order perturbation theory, is somewhat more general and may be written as

$$F(\vec{k}, \vec{k}+\vec{q}) = \sum_j f_j(\vec{k}, \vec{k}+\vec{q}) e^{-i\vec{q} \cdot \vec{r}_j}, \quad (2.53)$$

where F is the total scattering amplitude and f_j is the scattering amplitude associated with the site j , calculated exactly, rather than by the first order theory. It can be shown [see, e.g., Glauber (1961)] that as long as the total potential in the crystal can be associated with individual ionic sites, all we need to obtain (2.53) is to assume the validity of the weak scattering approximation i.e. to assume that the scattering from each site is small, small enough for multiple scattering to be neglected. It is not at all necessary to calculate the scattering from the individual sites by the Born approximation as we did in (2.49).

It is important to note an inconsistency in the application of (2.53) to the scattering of electrons in metals. It is clear from §2.3.2 that unless the Born approximation is valid, the potential due to screening

cannot be associated with the ionic sites at all. In view of this it is not clear, even in principle, how to go consistently beyond the first order theory.[†] If one is not satisfied with the results of the first order theory, the only option is to include higher order terms selectively. This is precisely what one does [see Meyer, Nester and Young (1967)], when one associates a potential with each ion site and calculate the total scattering from an exact estimate of f_j using (2.53) (or its counterparts which might include multiple scattering effects).

§2.5 Calculation of the Form Factors of a Pseudo-atom in a Pure Metal

Now we shall show how to calculate the form factors of a pseudo-atom in a pure metal. For the sake of concreteness, we shall take the Harrison pseudopotential as the

[†] Note that but for the conduction electrons the total scattering can in principle be calculated exactly (in practice, the only difficulty would be that we would need higher particle correlations to take into account multiple scattering effects).

basis of the calculation. For any other pseudopotential the method is similar.

Let us recall from §2.1 that for the Harrison pseudopotential $\langle \vec{k} + \vec{q} | W | \vec{k} \rangle$ is given by

$$\begin{aligned} \langle \vec{k} + \vec{q} | W | \vec{k} \rangle = & \langle \vec{k} + \vec{q} | V | \vec{k} \rangle + \sum_{\alpha} (k^2 + \langle \vec{k} | V | \vec{k} \rangle - E_{\alpha}) \langle \vec{k} + \vec{q} | \alpha \rangle \langle \alpha | \vec{k} \rangle \\ & + \sum_{\alpha} (k^2 + \langle \vec{k} | V | \vec{k} \rangle - E_{\alpha}) \langle \vec{k} | \alpha \rangle \langle \alpha | \vec{k} \rangle \frac{\langle \vec{k} + \vec{q} | P | \vec{k} \rangle}{1 - \langle \vec{k} | P | \vec{k} \rangle}, \end{aligned} \quad (2.54)$$

where, for convenience, we have changed to what we shall call the semiatomic units, obtained by putting $\hbar = 2m = \frac{1}{2}e^2 = 1$. In this system the unit of length is the Bohr radius, just as in the atomic units, and that of energy the Rydberg, which is half the atomic unit of energy. As in (2.51), making use of the separability of W , we get

$$\langle \vec{k} + \vec{q} | W | \vec{k} \rangle = (\vec{k} + \vec{q} | w | \vec{k}) S(\vec{q}), \quad (2.55)$$

with

$$\begin{aligned} (\vec{k} + \vec{q} | w | \vec{k}) = & (\vec{k} + \vec{q} | v | \vec{k}) + \sum_t (k^2 + \langle \vec{k} | V | \vec{k} \rangle - E_t) (\vec{k} + \vec{q} | t \rangle \langle t | \vec{k}) \\ & + \sum_t (k^2 + \langle \vec{k} | V | \vec{k} \rangle - E_t) (\vec{k} | t \rangle \langle t | \vec{k}) \frac{(\vec{k} + \vec{q} | p | \vec{k})}{1 - (\vec{k} | p | \vec{k})}, \end{aligned} \quad (2.56)$$

where p is given by

$$p = \sum_t | t \rangle \langle t |. \quad (2.57)$$

Evaluation of (2.56) is done in three steps:-

I. Evaluation of $(\vec{k} + \vec{q} | v^b | \vec{k})$.

II. Evaluation of $(\vec{k}+\vec{q}|w^R|\vec{k})$. This consists of the second and the third terms of (2.56) (the superscript R on w denotes "repulsive").

III. Evaluation of the screening of v^b and w^R . Note that since v consists of v^b and the screening of v^b , w^R should not have anything to do with the screening. Why, then, does the expression (2.39) for $w^S(q)$ involve w^b (which is the sum of v^b and w^R) and not v^b alone? The reason is obvious i.e. v^b being a deep potential, the calculation of its screening is difficult. So we fall back upon the assumption that the exact screening of v^b is reasonably well represented by the first order screening of w^b . In fact, this assumption and a similar assumption, namely, the exact scattering from v is reasonably well given by the first order scattering from w, constitute the whole spirit of the pseudopotential technique.

Finally, we add I, II and III to get $(\vec{k}+\vec{q}|w|\vec{k})$.

The potential v^b consists of four parts: $v_{(1)}^b$, $v_{(2)}^b$, $v_{(3)}^b$ and $v_{(4)}^b$, which denote, respectively, the potential due to the valence charge of the ion, the electrostatic potential due to the core, the potential due to conduction-core exchange, and the potential due to the conduction electrons (for reasons that will become clear later, $v_{(4)}^b$ is also called the potential due to the orthogonalization charge). If one is more

ambitious, one might include the potential due to the conductron-core correlation also, but it is usually small.

$v_{(1)}^b$ and $v_{(2)}^b$ can be calculated by noting that $\rho(\vec{r})$, the electron-density associated with an ion, is given by

$$\rho(\vec{r}) = \rho_c(\vec{r}) - (Z + n)\delta(\vec{r}) ,$$

where $\rho_c(\vec{r})$ is the density of electrons in the core and $(Z + n)$ is the charge on nucleus of the ion, Z being the valence of the ion and n the total number of the core electrons. The negative sign for the second term is due to the fact that the charge on the nucleus is of a sign opposite to that on an electron. Using Poisson's equation, (2.58) gives

$$(\vec{k}+\vec{q}|v_{1,2}^b|\vec{k}) = \frac{4\pi}{\Omega_0} \cdot \frac{2}{q^2} [\rho_c(\vec{q}) - Z - n], \quad (2.59)$$

where $v_{1,2}^b$ denotes the sum of $v_{(1)}^b$ and $v_{(2)}^b$ and $\rho_c(\vec{q})$ is given by

$$\rho_c(\vec{q}) = \int e^{-i\vec{q} \cdot \vec{r}} \rho_c(\vec{r}) d\vec{r} . \quad (2.60)$$

Note that the factor 2 in (2.59) arises from our use of Rydberg as the unit of energy.

$\rho_c(\vec{r})$ may be calculated from the wave functions of the core electrons since we have

$$\rho_c(r, \theta, \phi) = 2 \sum_{n, \ell, m} (1/r^2) P_{n\ell}^2(r) Y_{\ell m}^*(\theta, \phi) Y_{\ell m}(\theta, \phi) , \quad (2.61)^\dagger$$

where $(1/r)P_{n\ell}(r)$ denotes the radial part of the core wave function characterized by the quantum numbers n and ℓ .

Noting that

$$\sum_m Y_{\ell m}^*(\theta, \phi) Y_{\ell m}(\theta, \phi) = \frac{2\ell+1}{4\pi} ,$$

we get

$$\rho_c(r) = 2 \sum_{n, \ell} \frac{(2\ell+1)}{4\pi} \frac{1}{r^2} P_{n\ell}^2(r) , \quad (2.62)$$

so that

$$\rho_c(q) = \int \frac{\sin qr}{qr} U(r) dr , \quad (2.63)$$

where

$$U(r) = \sum_{n, \ell} 2(2\ell+1) P_{n\ell}^2(r) . \quad (2.64)$$

To obtain $v_{(3)}^b$, one uses the Slater approximation according to which the exchange potential due to like particles of density d is given by

$$-3e^2(3d/8\pi)^{1/3} \quad (\text{C.G.S. units}) . \quad (2.65)$$

Therefore, the potential due to conduction-core exchange in rydbergs would be

[†] The factor 2 in (2.61) arises from spin multiplicity.

$$-6(3\rho_c/8\pi)^{1/3},$$

whence

$$(\vec{k}+\vec{q}|v_{(3)}^b|\vec{k}) = -(1.2707/q)(4\pi/\Omega_0) \int \sin qr [rU(r)]^{1/3} dr, \quad (2.66)$$

where 1.2707 is value of $6(3/32\pi^2)^{1/3}$.

Now, regarding the conduction electron potential $v_{(4)}^b$, let us remind ourselves that as yet we are not considering the part of the conduction electron potential arising from the screening. This potential arises from a small nonuniformity, present irrespective of the screening, in the distribution of the conduction electrons. If the electron-density were uniform, there would be no $v_{(4)}^b$. But as a result of the orthogonalization of the conduction and the core states, this is not the case. The difference may be described by superposing on the uniform distribution an extra charge, localized in the core of each ion in the crystal. This charge is called the orthogonalization charge. Since the orthogonalization effectively modifies the charge on an ion and since the orthogonalization charge must be compensated by suitably modifying the uniform charge density which must now be different from what it would have been in the absence of the orthogonalization, the situation is the same as if the actual valence

Z is replaced[†] by an effective valence Z^* . The uniform density (of Z^* electrons in one atomic volume) does not contribute anything to $(\vec{k}+\vec{q}|\mathbf{v}^b|\vec{k})$, but the orthogonalization charge of $(Z^* - Z)|e|$ per ion, does. This latter contribution is represented by $v_{(4)}^b$. To determine $v_{(4)}^b$ we need to know Z^* and the manner in which the charge $(Z^* - Z)|e|$ is distributed.

It can be shown [Harrison (1966), pp. 271-2] that the orthogonalization charge per valence is given by

$$\langle\langle [\langle \vec{k} | P | \vec{k} \rangle (1 - \langle \vec{k} | P | \vec{k} \rangle)^{-1}] \rangle\rangle, \quad (2.67)$$

where $\langle\langle \rangle\rangle$ denotes the average of the enclosed expression over all the occupied states. Since (2.67) must be equal to $(Z^* - Z)/Z$, we get

$$Z^*/Z = \langle\langle [1 - \langle \vec{k} | P | \vec{k} \rangle]^{-1} \rangle\rangle. \quad (2.68)^*$$

[†] Note that as a result of orthogonalization, in (2.58) $(Z+n)$ would become $\{Z^* + [n + (Z - Z^*)]\}$, which is the same as before. This is as it should be because orthogonalization cannot be expected to change the charge on the nucleus

* Note from here that $Z^* > Z$ which is expected since orthogonalization leads to an exclusion of the conduction electrons from the region of the core.

Since for a pure metal $\langle \vec{k} | P | \vec{k} \rangle$ reduces to $(\vec{k} | p | \vec{k})$ and since we have

$$e^{i\vec{k} \cdot \vec{r}} = \sum_{\ell} [4\pi(2\ell+1)]^{\frac{1}{2}} i^{\ell} j_{\ell}(kr) Y_{\ell 0}(\theta, \phi) , \quad (2.69)$$

we get

$$\begin{aligned} Z^*/Z &= \langle\langle [1 - \sum_{n,\ell} A_{n\ell}(k)]^{-1} \rangle\rangle \\ &= \frac{\int_0^{k_F} \{1 - \sum_{n,\ell} [A_{n\ell}(k)]^2\}^{-1} 4\pi k^2 dk}{\int_0^{k_F} 4\pi k^2 dk} \\ &= 3 \int_0^1 dx x^2 \{1 - \sum_{n,\ell} [A_{n\ell}(xk_F)]^2\}^{-1} , \end{aligned} \quad (2.70)$$

where $A_{n\ell}$ is given by

$$A_{n\ell}(k) = (4\pi/\Omega_0)^{\frac{1}{2}} (2\ell+1)^{\frac{1}{2}} \int_0^{\infty} r j_{\ell}(kr) P_{n\ell}(r) dr . \quad (2.71)$$

The distribution of the orthogonalization charge can be shown to be given by [Harrison (1966)]

$$\begin{aligned} \langle\langle (1 - \langle \vec{k} | P | \vec{k} \rangle)^{-1} \{ \Omega^{\frac{1}{2}} e^{i\vec{k} \cdot \vec{r}} \sum_{\alpha} \psi_{\alpha}^* \langle \vec{k} | \alpha \rangle \\ + \Omega^{-\frac{1}{2}} e^{-i\vec{k} \cdot \vec{r}} \sum_{\alpha} \psi_{\alpha} | \vec{k} \rangle \\ - \sum_{\alpha, \beta} \psi_{\alpha}^* \psi_{\beta} \langle \vec{k} | \alpha \rangle \langle \beta | \vec{k} \rangle \} \rangle \rangle . \end{aligned} \quad (2.72)$$

To simplify the calculation we take the orthogonalization charge to have the same distribution as the core charge and in view of (2.72), this is not expected to be far from truth. With this approximation, $v_{(4)}^b$ is $(Z^* - Z)/n$ times

the potential due to the core charge. Therefore, by comparison with (2.59) we get

$$(\vec{k}+\vec{q}|v_{(4)}^b|\vec{k}) = -\frac{4\pi}{\Omega_0} \frac{2}{q^2} \frac{Z^*-Z}{n} \rho_c(q) . \quad (2.73)$$

The negative sign in (2.73) arises from a difference in the sign of the orthogonalization and the core charges.

This completes the evaluation of $(\vec{k}+\vec{q}|v^b|\vec{k})$. But before we proceed further, we note a point which will be found to be very useful later on. The expressions (2.59), (2.66) and (2.73) for the various parts of $(\vec{k}+\vec{q}|v^b|\vec{k})$ do not contain \vec{k} . Furthermore they depend upon \vec{q} only through its magnitude. (The first is a consequence of the fact that v^b is a local potential and the second arises from v^b being spherically symmetric.)

Now let us see how to determine $(\vec{k}+\vec{q}|w^R|\vec{k})$. We first discuss the evaluation of $(\vec{k}+\vec{q}|t\rangle\langle t|\vec{k})$. This should be straightforward by the use of (2.69). Allowance, however, has to be made for the fact that, in general, \vec{k} and $\vec{k}+\vec{q}$ are in different directions and since the specification of (θ, ϕ) in (2.69) is in polar coordinates with the Z-axis along \vec{k} , the expansion of $e^{i(\vec{k}+\vec{q})\cdot\vec{r}}$ will be in a different coordinate system. We take coordinates (θ_1, ϕ_1) based on \vec{k} and (θ_2, ϕ_2) based on $(\vec{k}+\vec{q})$. The core wave function $|t\rangle$ will be specified in coordinate system of \vec{k} . Thus we have

$$e^{i\vec{k} \cdot \vec{r}} = \sum_{\ell} [4\pi(2\ell+1)]^{\frac{1}{2}} i^{\ell} j_{\ell}(kr) Y_{\ell 0}(\theta_1, \phi_1)$$

$$e^{i(\vec{k}+\vec{q}) \cdot \vec{r}} = \sum_{\ell} [4\pi(2\ell+1)]^{\frac{1}{2}} i^{\ell} j_{\ell}(|\vec{k}+\vec{q}|r) Y_{\ell 0}(\theta_2, \phi_2)$$

$$\psi_t(\vec{r}) \equiv \psi_{n\ell m}(r) = (1/r) P_{n\ell}(r) Y_{\ell m}(\theta_1, \phi_1) .$$

Noting that the integrals over products of two $Y_{\ell m}$ vanish unless both have the same ℓ -value even if the coordinate systems are rotated with respect to each other, we get

$$\begin{aligned} & (\vec{k}+\vec{q}|t\rangle \langle t|\vec{k}) \\ &= (4\pi/\Omega_0)(2\ell+1) \left[\int dr r j_{\ell}(|\vec{k}+\vec{q}|r) P_{n\ell}(r) \int d\Omega Y_{\ell 0}^*(\theta_2, \phi_2) Y_{\ell m}(\theta_1, \phi_1) \right] \\ & \times \left[\int dr r j_{\ell}(kr) P_{n\ell}(r) \int d\Omega Y_{\ell m}^*(\theta_1, \phi_1) Y_{\ell 0}(\theta_1, \phi_1) \right] . \quad (2.74) \end{aligned}$$

The final angular integration gives δ_{m0} , which means we can put $m=0$ in the first angular integration also. The integral

$$\int d\Omega Y_{\ell 0}^*(\theta_2, \phi_2) Y_{\ell 0}(\theta_1, \phi_1) \quad (2.75)$$

may be evaluated by expressing $Y_{\ell 0}(\theta_1, \phi_1)$ in terms of $Y_{\ell m}(\theta_2, \phi_2)$ by the formula

$$Y_{\ell 0}(\theta_1, \phi_1) = \sum_m D_{m,0}^{\ell}(0, \theta, 0) Y_{\ell m}(\theta_2, \phi_2) , \quad (2.76)$$

where θ is the angle between the axes Z_1 and Z_2 or, in other words, it is the angle between \vec{k} and $\vec{k}+\vec{q}$. By the use of (2.76), the integral (2.74) becomes $D_{00}^{\ell}(0, \theta, 0)$ which is given by

$$D_{00}^{\ell}(0, \theta, 0) = \left(\frac{4\pi}{2\ell+1}\right)^{\frac{1}{2}} Y_{\ell 0}^{*}(\theta, 0) = P_{\ell}(\cos\theta) , \quad (2.77)$$

where P_{ℓ} is the Legendre Polynomial[†]. (2.74), then, simplifies to

$$(\vec{k}+\vec{q}|t\rangle \langle \vec{k}|) = A_{n\ell}(|\vec{k}+\vec{q}|)A_{n\ell}(k)P_{\ell}(\cos\theta) . \quad (2.78)$$

To complete the determination of w^R , we also require the value of $\langle \vec{k}|V|\vec{k}\rangle - E_{n\ell}$. For this we have

$$\langle \vec{k}|V|\vec{k}\rangle - E_{n\ell} = \bar{V} + |\epsilon_{n\ell}| - \Delta_{n\ell} , \quad (2.79)$$

where \bar{V} is the average potential experienced by a conduction electron in the crystal, $\epsilon_{n\ell}$ is the core energy of an (n, ℓ) -electron for an isolated ion and $\Delta_{n\ell}$ is the extra potential experienced by this electron when the ion is in the crystal. We shall treat $\epsilon_{n\ell}$ to be known (it can be determined either experimentally or, more usually, from a Hartree-Fock calculation). The next problem is to evaluate \bar{V} and $\Delta_{n\ell}$. Let us first calculate \bar{V} .

For this purpose one divides the crystal into Weigner Seitz (W.S.) cells. Since all the cells are equivalent, \bar{V} over the whole crystal is the same as \bar{V} over any one

[†] In this section, some symbols have been used for more than one quantities e.g. note the use of P in $P_{n\ell}$ and P_{ℓ} . This was done only in order to stick to the most widely used notation in each case, and it was felt that it will not give rise to any confusion.

W.S. cell. In this cell the total charge distribution consists of:

- (i) a nuclear charge $(Z+n)|e|$
- (ii) a core charge ne
- (iii) an orthogonalization charge $(Z^*-Z)|e|$
- (iv) a uniform electron density of total charge Z^*e .

Regarding (ii) we recall from our discussion of v^b that in addition to an electrostatic potential, it also gives rise to an exchange potential. We shall denote the electrostatic and the exchange contributions as (iia) and (iib) respectively.

In the point-ion approximation (i), (iia) and (iii) produce the same potential as a (point)charge $Z^*|e|$. The correction to (iia) due to the finite size of the core is just $v_{(2)}^b(r)$. The potential due to (iii) is also subject to a similar correction but we shall neglect this since it is much too small.

Now, since the contribution (iib) is clearly $v_{(3)}^b(r)$, we have

$$\bar{V} = v_{(2)}^b(q=0) + v_{(3)}^b(q=0) + \bar{V}_{\text{rest}} , \quad (2.80)$$

where the first two terms give the average of $v_{(2)}^b(r)$ and $v_{(3)}^b(r)$, and \bar{V}_{rest} denotes the average of the potential due to a point charge $Z^*|e|$ and a compensating electronic charge Z^*e distributed uniformly over the W.S. cell.

$v_{(3)}^b(q=0)$ may be immediately obtained from (2.66) and we get

$$v_{(3)}^b(q=0) = -(1.2707)(4\pi/\Omega_0) \int r [rU(r)]^{1/3} dr. \quad (2.66)'$$

For evaluating $v_{(2)}^b(q=0)$, we note from (2.59) that

$$\begin{aligned} v_{(2)}^b(q=0) &= \lim_{q \rightarrow 0} \left\{ -\frac{4\pi}{\Omega_0} \cdot \frac{2}{q^2} [\rho_c(q) - n] \right\} \\ &= \lim_{q \rightarrow 0} \left\{ -\frac{4\pi}{\Omega_0} \frac{2}{q^2} \left[n - \int \frac{\sin qr}{qr} U(r) dr \right] \right\}. \end{aligned}$$

Since

$$\int U(r) dr = n,$$

we immediately obtain

$$v_{(2)}^b(q=0) = \frac{4\pi}{3\Omega_0} \int r^2 U(r) dr. \quad (2.59)'$$

Assuming the W.S. cell to be a sphere, \bar{V}_{rest} is easily shown to be given by

$$\bar{V}_{rest} = -0.6 Z^*/r_0. \quad (2.81)$$

Here r_0 is the atomic sphere radius and is given by

$$r_0 = (3\Omega_0/4\pi)^{1/3}. \quad (2.82)$$

This completes the evaluation of \bar{V} . Now we come to the calculation of Δ . If we again divide the crystal into W.S. cells, the only contribution to the potential will come from the cell in which the ion under study is situated. The other cells being neutral, do not contribute. In the W.S. cell of the ion we again have the various charges (i),

(ii), (iii) and (iv). But now we do not have to worry about (i) and (ii) because their effect is already contained in $\epsilon_{n\ell}$. The excess potential that the electron experiences by the ion being in the crystal compared to the case of the isolated ion is only due to (iii) and (iv). Therefore, $\Delta_{n\ell m}$ (using the approximations made earlier in this section, we shall show presently that depends only on n and ℓ) is given by

$$\Delta_{n\ell m} = \int [v^{oc}(\vec{r}) + v^{cc}(\vec{r})] [P_{n\ell}^2(r)/r^2] Y_{\ell m}^*(\theta, \phi) Y_{\ell m}(\theta, \phi) d\vec{r} , \quad (2.83)$$

where v^{oc} and v^{cc} are respectively the potentials due to the orthogonalization charge and the conduction charge. As in v^b , we assume the orthogonalization charge to be having the same distribution as the core charge and as in \bar{V} , we take the W.S. cell to be a sphere. Then we have

$$v^{oc}(\vec{r}) = v^{oc}(r) = - \frac{2(Z^* - Z)}{n} \left[\frac{1}{r} \int_0^r U(r') dr' + \int_0^\infty \frac{U(r')}{r'} dr' \right] \quad (2.84)$$

and

$$v^{cc}(\vec{r}) = v^{cc}(r) = \frac{Z^*}{r_0} \left[3 - \left(\frac{r}{r_0} \right)^2 \right] . \quad (2.85)$$

Since $v_{cc}(r)$ varies rather slowly with r , following Harrison, we approximate $v_{cc}(r)$ by its value at $r=0$. However, $v^{oc}(r)$ varies much more rapidly with r and we

cannot make the same approximation in this. Thus from (2.82), we have

$$\Delta_{n\ell} = \frac{3Z^*}{r_0} + \Delta_{n\ell}^{oc}, \quad (2.86)$$

with $\Delta_{n\ell}^{oc}$, the contribution to $\Delta_{n\ell}$ from the orthogonalization charge, being given by

$$\Delta_{n\ell}^{oc} = \int v^{oc}(r) P_{n\ell}^2(r) dr. \quad (2.87)$$

(2.86), with (2.87) and (2.84) determines $\Delta_{n\ell}$.

This finishes the evaluation of $(\vec{k}+\vec{q}|w^R|\vec{k})$. It is useful to note that, unlike $(\vec{k}+\vec{q}|v^b|\vec{k})$, it depends on both \vec{k} and $\vec{k}+\vec{q}$ and not on q alone (this is because, as noted in §2.1, w^R is nonlocal). However, from (2.56) and (2.78) it may be seen that this dependence reduces to the dependence on q , k and $|\vec{k}+\vec{q}|$. Thus the vector triangle of \vec{k} , \vec{q} and $\vec{k}+\vec{q}$ may be rotated in space without affecting the value of $(\vec{k}+\vec{q}|w^R|\vec{k})$. This in fact would be true, see Harrison (1966) p. 20, for all w^R for which $f(\vec{k}, t)$ depends only on the magnitude of \vec{k} which is, of course, true for the Harrison pseudopotential.

Now let us discuss the screening. For simplicity we shall discuss Hartree screening and will take the electron mass to be the same as its free mass. As discussed in §2.3.2, the expressions thus obtained can easily be modified to include the effect of exchange and the influence of the effective mass.

Modifying (2.39) for the change of units and remembering that now our plane waves are normalized over Ω_0 instead of Ω , we get

$$w^S(\vec{q}) = \frac{4}{\pi^2 q^2 \epsilon(q)} \left[\int \frac{d\vec{k}(\vec{k}+\vec{q}|v^b|\vec{k})}{k^2 - |\vec{k}+\vec{q}|^2} + \int \frac{d\vec{k}(\vec{k}+\vec{q}|w^R|\vec{k})}{k^2 - |\vec{k}+\vec{q}|^2} \right]. \quad (2.88)$$

Both the integrals in (2.88) contain a singularity at $k=|\vec{k}+\vec{q}|$. We want to find the principal values of these integrals. The first term does not present any difficulty since $(\vec{k}+\vec{q}|v^b|\vec{k})$ can be taken outside the integration sign and the rest of the integral can be evaluated analytically. However, the same does not apply to the second term and we have to evaluate the integral numerically taking the singularity into account. Let us postpone our worries for the time being and just denote the second integral by I . This gives

$$w^S(q) = v^b(q) \frac{1-\epsilon(q)}{\epsilon(q)} + \frac{4}{\pi^2 q^2 \epsilon(q)} I(q). \quad (2.89)$$

Note that w^S depends only on the magnitude of \vec{q} because from the foregoing discussion we know that

$$(\vec{k}+\vec{q}|v^b|\vec{k}) = v^b(q)$$

and

$$(\vec{k}'|w^R|\vec{k}) = w^R(q, k, k'),$$

where $\vec{k}' = \vec{k} + \vec{q}$.

Adding the matrix element of w^b to (2.88), the form factor of the total screened pseudopotential is found to be

$$(\vec{k}' | w | \vec{k}) = w(q, k, k') = \frac{v^b(q)}{\epsilon(q)} + w^R(q, k, k') + \frac{4}{\pi^2} \frac{I(q)}{q^2 \epsilon(q)} \quad (2.90)$$

Note that the screened form factor of v^b is given simply by dividing the bare form factor $v^b(q)$ by the dielectric function $\epsilon(q)$. This is a standard result for a local potential and will not apply to w^R , since w^R is nonlocal. However, in the so-called semilocal approximation, the nonlocal nature of w^R is ignored for the purposes of the calculation of the screening. In that case we get

$$w(q, k, k') = \frac{v^b(q) + w^R(q, k, k')}{\epsilon(q)} \quad (2.91)$$

semilocal approximation.

In the full nonlocal theory we cannot use (2.91) and must try to evaluate the principal value of $I(q)$ and determine the form factors of w from (2.90). The discussion of the evaluation of $I(q)$ is given in Appendix I.

To facilitate the writing of a computer program, we summarize below the various steps in the evaluation of the pseudopotential form factors:-

1. Data

Ω_0 for the metal,

Z , $P_{n\ell}(r)$ and $\epsilon_{n\ell}$ for the ion. (The last two are usually obtained from the Hartree-Fock calculations.)

2. Using $P_{n\ell}$, obtain $U(r)$ from (2.64) and obtain Z^*/Z from (2.70) and (2.71).

3. (i) Using (2.63), obtain $\rho_c(q)$ from $U(r)$ and substituting for Z^*/Z , obtain $v_{1,2,4}^b$ from

$$v_{1,2,4}^b = \frac{4\pi}{\Omega_0} \cdot \frac{2}{q^2} \{-Z - n + \rho_c(q) [1 - \frac{Z^* - Z}{n}]\},$$
 which is the sum of (2.59) and (2.73).
 - (ii) Using (2.66), obtain $v_3^b(q)$ from $U(r)$.
 - (iii) Calculate $\epsilon^*(q)$ or $\epsilon(q)$ from (2.46) or (2.35) depending on whether or not the effect of exchange on screening is to be included.
 - (iv) Add $v_{1,2,4}^b(q)$ and $v_3^b(q)$, and divided by $\epsilon^*(q)$ or $\epsilon(q)$, as the case may be, to get $v(q)$, the screened form factor of v^b .
4. (a)(i) Use $U(r)$ in (2.59)' and (2.66)' to get $v_2^b(q=0)$ and $v_3^b(q=0)$.
 - (ii) Substitute these in (2.80) to get \bar{V} with the help of (2.81) and (2.82).
- (b) (i) Evaluate $v^{oc}(r)$ from (2.84).
 - (ii) Substitute in (2.86) to get $\Delta_{n\ell}^{oc}$, and
 - (iii) Use (2.86) to get $\Delta_{n\ell}$.
- (c) Obtain $\langle \vec{k} | V | \vec{k} \rangle - E_{n\ell}$ from (2.79).
5. Calculate $(\vec{k} + \vec{q} | t \rangle \langle t | \vec{k})$ from (2.71) and (2.78).
6. Substitute $\langle \vec{k} | V | \vec{k} \rangle - E_{n\ell}$ and $(\vec{k} + \vec{q} | t \rangle \langle t | \vec{k})$ in the last two terms of (2.56) to get w^R .
7. Evaluate $I(q)$ and obtain $w(q, k, k')$ from (2.90) or use (2.91) if one does not mind the use of the semi-local approximation.

It may be mentioned that a pseudopotential calculation with nonlocal screening takes much longer as compared to a similar calculation using the semilocal approximation. The actual amount of extra computer time depends upon the complexity of the ion under consideration: For Li, nonlocal screening takes 3 times longer and for Zn about 10 times longer. Yet, in view of the high accuracy demanded of the calculation of the form factors to be used for obtaining the resistivity [see, e.g., Wiser (1966)], it appears to be worthwhile to go through the trouble of calculating the screening nonlocally.

§2.6 Critique of the Pseudopotential Method

In spite of an impressive record of success in explaining a wide range of the properties of metals, there are certain features of the theory of pseudopotentials which make one feel uncomfortable about the whole thing. One is the lack of a suitable criterion for selecting a pseudopotential. Should one try to have the smoothest wave function or the smoothest potential or the most rapid convergence of the Born series? Another and perhaps by far the most serious one is that while with a suitably chosen pseudopotential, first order calculations of the scattering may be reasonably accurate, it is not clear how to proceed to higher orders consistently. It may be noted

that if we knew how to calculate the higher orders, the absence of a criterion for choosing would not have mattered since any choice would give the same final result in an exact calculation.

But then, the importance of the method of pseudopotentials lies not in that it leads to a rigorous concept but in that it is a very fertile approximation. Before the advent of pseudopotentials, the total potential being strong, one was required to work with the perturbing potential, and for every new situation, a new postulate was required for its calculation. Now we can deal directly with the total potential, the scattering due to which is known as soon as we have calculated the pseudopotential of the ions involved and have determined the arrangement of ions by some means, say the neutron or the X-ray scattering. The technique applies no matter whether we want the scattering due to dislocations, thermal vibrations, impurities and what have you. The question of postulating the perturbing potentials in different situations just does not arise.

PART II

RESISTIVITY DUE TO IMPURITIES

Chapter 3

PSEUDOPOTENTIALS IN ALLOYS AND THE CALCULATION OF THE RESIDUAL RESISTIVITY*

§3.1 Preliminary Remarks

As we stated in the Introduction, the pseudopotential form factors of an ion depend on its environment. In this chapter we first briefly review Harrison's (1966) calculations for the form factors in an alloy. Then we discuss the improvements that are necessary and calculate the matrix elements afresh. In §3.3 we use the matrix elements to calculate the residual resistivity ρ_r of a dilute alloy. We shall see that our results differ substantially from those given by Harrison. Further, when allowance is made for the effective mass factor and nonlocal screening, our calculated results are in satisfactory agreement with experiment.

Calculations for some alloys, not considered by Harrison, are also presented.

§3.2 Calculation of the Form Factors in an Alloy

§3.2.1 Harrison's Theory

Harrison suggested that the form factors in an alloy can be calculated by applying the correction for the

* The results described in this chapter have been published in Gupta (1968).

changes in the dielectric constant $\epsilon(q)$ and the atomic volume Ω_0 . Both of these are simple to apply and we get the following relation between the form factors of an ion in an alloy and those of the same in the pure metal:

$$[w(q)]_{\text{alloy}} = [w(q)]_{\text{p.m.}} \frac{[\epsilon(q) \cdot \Omega_0]_{\text{p.m.}}}{[\epsilon(q) \cdot \Omega_0]_{\text{alloy}}} , \quad (3.1)$$

where the subscript p.m. stands for pure metal.

If one wants to use this scheme for calculating the form factors of an ion for a number of different conditions of alloying (achieved either by changing the metal with which it is alloyed or by changing the concentration), the calculations may be simplified by using the point-ion model for the potential of the ion. In this model the unscreened pseudopotential is represented by

$$w^b(r) = - \frac{2Z}{r} + \beta \delta(r) , \quad (3.2)$$

where Z is the valence of the ion and β the point-ion parameter determined by adjusting its value such that the screened form factors

$$\left(- \frac{8\pi Z}{q^2} + \beta \right) / \Omega_0 \epsilon(q) \quad (3.3)$$

agree with the calculated form factors. (As in chapter 2, the units we are using here are the semiatomic units $\hbar=2m=\frac{1}{2}e^2=1$). Once the form factors for the pure metal have been calculated, β can be determined and the form factors for any situation may, then, be obtained from (3.3).

It may be mentioned that the results obtained from (3.3) have very nearly the same accuracy as those obtained from (3.1) since the single parameter β gives a rather good fit to the calculated form factors, particularly for the set of form factors needed in resistivity (i.e., q ranging from 0 to $2k_F$ and both k and k' equal to k_F).

Harrison applied this theory to the calculation of the form factors in dilute alloys. In such alloys the form factors of the host may be taken to be unchanged and for calculating the form factors of the impurity, $[\Omega_0 \epsilon(q)]_{\text{alloy}}$ may be taken to be equal to $[\Omega_0 \epsilon(q)]_{\text{pure host}}$. When these form factors were used for determining ρ_r , agreement with experiment was found to be poor.

§3.2.2 A Closer Look at the Form Factors of an Ion in an Alloy

Compared to the case of an ion in the pure metal, the ion in an alloy notices three important changes that have a bearing on its form factors:

- (a) change in Ω_0 ,
- (b) change in the electron density surrounding the ion, and
- (c) change in the other ions among which the ion is placed.

(a) comes into the picture because the states $|\vec{k}\rangle$ and $|\vec{k}+\vec{q}\rangle$ characterizing a form factor, are normalized

to unity over Ω_0 . The effect of this change is easy to take into account and it is clear from (3.1) how to do it.

The effect of (b) and (c) is more complex in nature. They lead to a shift in Δ , the zero of the energy in the crystal relative to the free ion, to a change in k_F and to a change in the orthogonalization charge. Of these, the change in k_F is brought about by (b) alone, that in the orthogonalization charge and Δ by both (b) and (c). All these three, notably Δ and k_F , are important parameters in a pseudopotential calculation.

The reason why Δ enters the calculation of the form factors is that to determine the scattering from an ion in the crystal, we must use the data relevant to the ion in the crystal. Since we do not possess these data, we deduce them from the corresponding results for the free ion. As discussed in chapter 2, the difference between the two situations may be described to a good approximation by a shift Δ in the core energies while the wave function may be taken to be unchanged. The extent of the influence of Δ on the form factors has been clearly brought out by Lin and Phillips (1965). They conclude that a change in Δ by 0.1 ryd changes the form factors by 0.01 ryd, which is the accuracy to which one tries to determine the form factors. (It may be mentioned that the shift in Δ on alloying is usually from 0.3 to 0.5 ryd.)

Regarding how the form factors are influenced by k_F , one point is obvious, i.e., through the effect of k_F on the potential due to screening. This, of course, has been taken into account by Harrison. (It hardly needs to be mentioned that changing $\epsilon(q)$, as done by Harrison, takes care of the change in the potential due to screening only in the semilocal approximation.) But when one is interested in such properties (like electrical resistivity) as depend upon the matrix elements of the potential with one or both the states lying on the Fermi surface, k_F enters in yet another way. The pseudopotential being nonlocal, the matrix elements involve not only q but also k_F . The importance of taking both the initial and the final momentum (and not just the transfer of momentum) into account for the calculation of pseudopotential matrix elements can hardly be over-emphasized in view of the work of Animalu (1965) and of Animalu and Heine (1965) who obtained considerably improved agreement with experiment over the earlier treatments, which had ignored this in the calculation of the screening.

Thus when Δ and k_F change, as they do on alloying because of (b) and (c), we cannot expect the new form factors to be related to the previous ones in a simple manner. A proper account of this change can be taken only by making a fresh calculation with the changed values of these quantities. The effect of the change

of orthogonalization charge is not likely to be very significant. But in view of the high accuracy in the form factors demanded for the resistivity calculations [see Wiser (1966)], it is advisable to include this also.

It may be parenthetically pointed out that the above remarks about the effects of Δ , k_F etc. on the form factors are by no means restricted to the pseudopotential approach. They apply equally well, no matter which of the various formulations of the effective potential theory, the pseudo-, the model[†] and the quasipotential, one chooses as the basis of the calculation.

Below we shall obtain an explicit expression for the form factors of an ion in an alloy from the Harrison pseudopotential. We shall consider the case of a dilute alloy, dilute enough for the impurity to be regarded as isolated. As mentioned before, in this situation the only problem is to calculate the form factors of the impurity; those of the host may be taken to be unchanged by alloying. Our reason for using the Harrison pseudopotential as the basis of the calculations is that by comparing our results for residual resistivity with those of Harrison, the importance of taking into account the changes on alloying

[†] The dependence of the model potential on Δ is, perhaps, not very obvious so that it may be useful to mention that it arises from the dependence of A_ℓ , the parameters of the model potential, on Δ .

in Δ , k_F etc. in the calculation of the form factors, can be clearly appreciated.

§3.2.3 Impurity Form Factors in a Dilute Alloy from the Harrison Pseudopotential

The matrix element of Harrison's optimized and linearized total pseudopotential W is given (in rydbergs) by (2.54). As before (§2.3), on writing the core states $|\alpha\rangle$ as $t_j(\vec{r}-\vec{r}_j)$, where t_j denotes the t -th core state of the ion occupying the position \vec{r}_j , and on using the usual assumptions that the screening is linear and that the core energies of an ion depend only on the specie of the ion (i.e., they are independent of the location of the ion in the crystal), from (2.54) we get

$$\langle \vec{k}+\vec{q} | W | \vec{k} \rangle = N^{-1} \sum_j e^{-i\vec{q} \cdot \vec{r}_j} (\vec{k}+\vec{q} | w_j | \vec{k}) , \quad (3.4)$$

with

$$\begin{aligned} (\vec{k}+\vec{q} | w_j | \vec{k}) &= (\vec{k}+\vec{q} | v_j | \vec{k}) \\ &+ \sum_{t_j} [k^2 + \langle \vec{k} | V | \vec{k} \rangle - E_{t_j}] A_{t_j}(|\vec{k}+\vec{q}|) A_{t_j}(k) P_\ell(\cos\theta) \\ &+ \{ N^{-1} \sum_{j, t_j} \frac{[k^2 + \langle \vec{k} | V | \vec{k} \rangle - E_{t_j}] [A_{t_j}(k)]^2}{1 - \langle \vec{k} | P | \vec{k} \rangle} \} \\ &\times \sum_{t_j} A_{t_j}(|\vec{k}+\vec{q}|) A_{t_j}(k) P_\ell(\cos\theta) , \end{aligned} \quad (3.5)$$

where A_{t_j} is given by (2.70). The factor $P_\ell(\cos\theta)$, where

θ is the angle between \vec{k} and $\vec{k}+\vec{q}$, arises (see §2.5) from the projection of $|t_j\rangle$ on two plane waves $|\vec{k}\rangle$ and $|\vec{k}+\vec{q}\rangle$ propagating in directions which are, in general, different.

We notice from (3.5) that, in general, the form factors of an ion in an alloy depend upon the nature and concentration of the constituents. The situation simplifies considerably for a dilute alloy. For this, the form factors of the host are left unchanged. For the impurity we get*

$$\begin{aligned}
 (\vec{k}+\vec{q}|w|\vec{k}) &= (\vec{k}+\vec{q}|v|\vec{k}) \\
 &+ \Sigma_t [k^2 + \langle \vec{k}|V|\vec{k}\rangle - E_t] A_t(|\vec{k}+\vec{q}|) A_t(k) P_\ell(\cos\theta) \\
 &+ \Sigma_t, \frac{[k^2 + \langle \vec{k}|V|\vec{k}\rangle - E_t] [A_t(k)]^2}{1 - \Sigma_t'' [A_t''(k)]^2} \\
 &\times \Sigma_t A_t(|\vec{k}+\vec{q}|) A_t(k) P_\ell(\cos\theta) . \tag{3.6}
 \end{aligned}$$

The method of evaluation of (3.6) runs parallel to the evaluation of (2.56) for the pure metal. Here we shall go over the various steps indicating the changes, where necessary, caused by alloying. For the details of the

* Note that except for quantities like Ω_0 which are obviously for the host, all expressions not carrying the subscript host are to be evaluated for the impurity ion.

steps involved, one may refer to §2.5 (the notation used here is the same as there).

First let us consider the part $(\vec{k}+\vec{q}|v|\vec{k})$ of (3.6). This is equal to the sum of the bare potential and the potential due to screening of the sum of the true and the repulsive potentials. The bare true potential and its screening add up to give $v^b(q)/\epsilon(q)$ and the screening of the repulsive part is given by $4 I(q)/\pi^2 q^2 \epsilon(q)$. Therefore, we get

$$(\vec{k}+\vec{q}|v|\vec{k}) = v^b(q)/\epsilon(q) + 4 I(q)/\pi^2 q^2 \epsilon(q) . \quad (3.7)$$

The potential v^b consists of four parts: $v_{(1)}^b$, $v_{(2)}^b$, $v_{(3)}^b$ and $v_{(4)}^b$, which denote, respectively, the potential due to the valence charge of the ion, the electrostatic potential of the core, the potential due to conduction-core exchange and the potential due to the orthogonalization charge. Since the Fourier transforms of the first three depend upon alloying only through Ω_0 , these can be evaluated directly using (2.59) and (2.66). Regarding $v_{(4)}^b$, we note from (2.67) and (2.72) that both the magnitude and the distribution of the orthogonalization charge per valence charge of an ion depend not only on the ion itself but on (the core wave functions of) all the ions in the crystal. Therefore, for a dilute alloy we have

$$v_{(4)}^b(q) = (Z/Z_{\text{host}}) [v_{(4)}^b(q)]_{\text{host}} . \quad (3.8)$$

For the evaluation of the last two terms of (3.6) we observe that the average potential in crystal $\langle \vec{k} | V | \vec{k} \rangle$ will be the same as in the absence of the impurity. Therefore, from (2.80) and (2.81) we get

$$\langle \vec{k} | V | \vec{k} \rangle = [-0.6Z^*/r_o + v_{(2)}^b(o) + v_{(3)}^b(o)]_{\text{host}}. \quad (3.9)$$

The core energies of the impurity ion in the crystal are given by

$$\begin{aligned} E_t &\equiv E_{n\ell} \\ &= -|\epsilon_{n\ell}| + \Delta_{n\ell}, \end{aligned} \quad (3.10)$$

where $\Delta_{n\ell}$ is given by [see eqns. (2.85) and (2.86)]

$$\Delta_{n\ell} = 3Z^*/r_o + \int v^{oc}(r) P_{n\ell}^2(r) dr. \quad (3.11)$$

For obtaining $v^{oc}(r)$, we use the same argument as we did for obtaining $v_{(4)}^b(q)$ above. This gives

$$v^{oc}(r) = (Z/Z_{\text{host}}) [v^{oc}(r)]_{\text{host}}. \quad (3.12)$$

In view of the above changes, the outline of the complete procedure for determining the impurity form factors in a dilute alloy would be:

1. Determine $v_{1,2}^b$ from (2.59) and v_3^b from (2.66) using wave functions $P_{n\ell}(r)$ of the impurity but Ω_o of the host.
2. Calculate $[v_{(4)}^b(q)]_{\text{host}}$ from (2.72) and thence obtain $v_{(4)}^b(q)$ for the impurity from (3.8).

3. (i) Calculate $[-0.6Z^*/r_o + v_{(2)}^b(o) + v_{(3)}^b(o)]_{\text{host}}$
and $[v^{oc}(r)]_{\text{host}}$.
- (ii) Determine $[\langle \vec{k} | V | \vec{k} \rangle - E_t]$ from (3.9) to (3.12).
- (iii) Substitute this and the impurity wave functions in (3.6) to obtain $w^R(q, k, k')$.
4. Using $v^b(q)$ and $w^R(q, k, k')$ obtained above, determine $(\vec{k} + \vec{q} | v | \vec{k})$ from (3.7), where $I(q)$ is given by (2.88).
Note that at the step 4 and, in most cases[†], also at 3(iii), we require the value of k_F . The k_F to be used here is clearly that of the host.

Further details of the above steps may be found on pp.54-55 of the thesis. For the sake of completeness, a copy of the matrix elements calculated by us is appended to the thesis.

§3.3 Calculation of the Residual Resistivity and Discussion of the Numerical Results

Once the matrix elements are known the calculation of the residual resistivity is elementary. The probability of scattering $P(\vec{k}, \vec{k}')$ by N_c impurities (N total number of

[†] The cases for which 3(iii) involves k_F have been mentioned before i.e. where, as in the calculation of the resistivity, one requires the value of $(\vec{k} + \vec{q} | w | \vec{k})$ with at least one of k and $|\vec{k} + \vec{q}|$ being equal to k_F .

atoms in the crystal), when $c \ll 1$, is given by

$$P(\vec{k}, \vec{k}') = \frac{2\pi c}{\hbar N} [w_A(q, k, k') - w_B(q, k, k')]^2 \delta(E_k - E_{k'}) , \quad (3.13)$$

where A and B denote the host and the impurity atoms, and $\vec{q} = \vec{k}' - \vec{k}$. Substituting (3.13) in (1.8) and assuming E-k relation to be parabolic, we get

$$\frac{1}{\tau_{k_F}} = \frac{m^* \Omega_o k_F c}{2\pi \hbar^3} \int (1 - \cos\theta) [w_A^F(q) - w_B^F(q)]^2 \sin\theta d\theta, \quad (3.14)$$

where Ω_o is the volume per atom and $w^F(q)$ stands for $w(q, k_F, k_F)$. From (3.14) and (1.16), we get for ρ_r^o , the residual resistivity per atomic per cent of the impurity, the expression

$$\rho_r^o = \frac{3\pi(m^*)^2 \Omega_o}{400 e^2 \hbar^3 k_F^2} \int_0^2 [w_A^F(x) - w_B^F(x)]^2 x^3 dx , \quad (3.15)$$

where $x = q/k_F$.

Numerical calculations of ρ_r^o were undertaken with two objects in view. The first was to study the effect on ρ_r^o due only to the modifications of the impurity form factors discussed in §3.2.2 and §3.2.3 because while there is no doubt that these modifications should be taken into account, it is, after all, not very meaningful to go through all the trouble involved in trying to include them if their effect is going to be small. The second object was to see if by incorporating some further improvements, it is possible to get a reasonable agreement with experimental residual resistivities.

To serve the first objective, one set of calculations was performed where, while the modifications proposed in §3.2.2 and §3.2.3 were included, the treatment was otherwise similar to that of Harrison (local screening and $m^*=m$). The results of these calculations are given in column A of the "Present calculations" in Table I. The alloys treated here are those for which Harrison obtained the residual resistivities from first principles.* The difference between the results in A and those of Harrison is due only to the changes by alloying in Δ , k_F etc. From a comparison of the results it is clear that these changes exert an important influence on the form factors: Taking this into account in the calculation of the form factors of an isolated impurity can change the residual resistivity by as much as a factor of 4 or more.

After the importance of the proposed modifications was established, we tried to improve the set A from two points of view: first, by treating the screening nonlocally including the effect of exchange and secondly,

* Harrison calculated ρ_r^0 for a number of other alloys also by adjusting his parameter β to optimize agreement with experiment.

Table I. Residual resistivities for the alloys treated by Harrison from first principles. All the values are in $\mu\Omega$ cm.

Host	Alloy purity	Harrison	Present calculations				Experiment
			A	B	C	D	
Al	Mg	0.78	0.17	0.23	0.23	0.28	0.33
	Zn	0.1	0.13	0.14	0.14	0.17	0.22
	Ca	1.8	3.1	4.5	4.1	4.9	>4.5
Mg	Al	1.6	0.63	0.82	0.83	1.0	2.1
	Li	0.27	0.33	0.44	0.58	0.69	0.75

by taking into account the influence of the effective mass. Column B in Table I gives the results incorporating the first improvement. The role played by effective mass has two aspects. One is connected with its influence through the screening and the Fermi energy. The calculations taking this into account are given in C. The other aspect relates to the multiplication of the resistivities obtained by using the free-electron density of states, by $(m^*/m)^2$. The set D represents the results after this multiplication. The effective masses used for obtaining the sets C and D were taken from the work of Animalu and Heine (1965).

Table I shows that while the single most important factor to which the poor agreement of Harrison's results may be attributed is his neglect of the influence of the changes in Δ , k_F etc. for the impurity ion, the agreement

with experiment improves as successive stages of refinements are incorporated. It is gratifying to note that except for the case of Al in Mg, the set D reproduces the experimental resistivities within 20%. We are not clear what gives rise to the rather large discrepancy for this alloy. It is possible that this is due to the occurrence of resonance scattering [see, e.g., Ziman (1964)], in which case our estimate will naturally be much lower than the correct value.

We may draw attention to the fact that in our treatment, multiplication by the somewhat controversial factor $(m^*/m)^2$ consistently leads to a better agreement with experiment; see discussion on p.10.

Resistivities of dilute alloys of Alkali Metals

Recently Dickey, Meyer and Young (1967) have calculated the residual resistivities of alloys of monovalent metals containing monovalent impurities using the quasipotential form factors obtained from the phase-shift data of Meyer, Nestor and Young (1967) (abbreviated hereafter as MNY). The phase shifts used for every ion are relevant to the appropriate k_F so that in this work the dependence of the form factors on k_F is automatically taken care of. Because of the interesting connection between the influence of k_F on the quasi-

potential form factors and the nonlocal nature of the pseudopotential, we decided to perform calculations for alloys made from the combinations of Li, Na and K to see how our results compare with those of Dickey et al.

Table II. Residual resistivity for the alloys obtained from combinations of Li, Na, and K. All the values are in $\mu\Omega$ cm.

Alloy		Dickey et al.	Present calculations			Experi- ment
Host	impurity		B	C	D	
Li	Na	0.47	0.02	0.24	0.43	
	K	5.69	2.1	0.79	1.4	
Na	Li	0.33	0.00	0.04	0.05	
	K	1.55	2.0	1.3	1.6	
K	Li	0.50	1.7	3.7	2.9	
	Na	0.67	2.0	3.4	2.6	0.56

The results of these calculations are given in Table II. The calculations corresponding to column A of Table I have been omitted here and those given in B, C, and D have the same significance as before. The effective masses used in C and D are taken from Ham (1962). Since Dickey et al. have not considered the influence of the effective mass, their results should be compared with our set B. However, our best estimate is represented by the set D.

From Table II we note that (a) the results in column B do not compare well with those of Dickey et al. and (b) except in the case of two alloys, Na in Li and K in Na, our best estimates also differ considerably from the results of Dickey et al.

To provide at least a partial understanding of (a) we would like to draw attention to certain results obtained by Young, Meyer and Kilby (1967). They found that for Li^+ in the MNY phase shifts at the k_F for lithium gave a rather large resistivity* for the liquid metal ($93.3 \mu\Omega \text{ cm}$ compared to the experimental value 24.0). Further, they found that the agreement is much better if a modified potential is used which yields the phase shifts 0.434 , 0.352 , 0.015 and 0.001 instead of MNY phase shifts 0.242 , 0.417 , 0.015 and 0.001 . On using the modified phase shifts for Li^+ , we get 0.06 and $4.8 \mu\Omega \text{ cm}$ for ρ_r^0 of Na in Li and K in Li, respectively (note that the modified phase shifts being evaluated at the k_F for lithium, these are the only two alloys in Table II for which they can be used). Keeping in mind the reliability of the second decimal place in these calculations, for Na in Li the new value may be seen to compare well with the value

* The same applies to Na and K, but to a lesser extent. The MNY phase shifts give 17.0 and $27.5 \mu\Omega \text{ cm}$, compared with the experimental values 9.65 and 13.2 .

in column B. The difference remains large for K in Li, though the gap is slightly reduced.

As regards (b), experimental work is necessary to determine which results are closer to the correct value. It may be mentioned that the agreement with experiment obtained by Dickey et al. for the alloy Na in K may be fortuitous. This is because Na and K atoms have a tendency to form $(\text{Na}_2\text{K})^+$ ion and this would affect the resistivity.

§3.4 Summary

We have emphasized the role of the surroundings in the form factors of an ion. When they change, as they do on alloying, Harrison's recipe is too inadequate to take into account the effect of their change, because of the accompanying changes in the Fermi momentum, the position of the zero of the energy in the crystal relative to that for the free ion, and the orthogonalization charge. These can be taken into account only by doing the whole calculation all over again. On using the form factors obtained by such a calculation for determining the residual resistivity, we are led to a considerably better agreement with experiment than obtained by Harrison except for the alloy Al in Mg. That our results for the alloys obtained from combinations of Li, Na, and K differ considerably from those of Dickey et al. should not be disturbing, in

view of the large divergences between the experimental values for the resistivities of (pure) liquid Li, Na, and K and those obtained from the MNY phase shifts employed by Dickey et al. It will be of interest to have the experimental results for these alloys.

Chapter 4

DEVIATIONS FROM MATTHIESSEN'S RULE

§4.1 Theoretical Basis of Matthiessen's Rule
and Introductory Remarks

The derivation of Matthiessen's rule employs two assumptions which are:-

A. The probability P_i of scattering due to the host lattice and P_r that due to the impurity atoms, considered at rest, are additive i.e., the total probability of scattering is given by

$$P = P_i + P_r \quad . \quad (4.1)$$

B. The trial function $\phi_{\vec{k}}$ in (1.17) for the alloy is taken to be proportional to the trial function $\phi_{\vec{k}}^i$ for the host lattice. In other words

$$\phi_{\vec{k}} = a \phi_{\vec{k}}^i = b \phi_{\vec{k}}^r \quad , \quad (4.2)$$

where $\phi_{\vec{k}}^r$ is the trial function when P_r alone is present, and a and b are constants (independent of \vec{k}). (4.2) is a valid assumption if relaxation times can be defined for both P_i and P_r and if their ratio is independent of the direction of \vec{k} .

The total resistance ρ of a dilute alloy is usually written as

$$\rho = \rho_i + \rho_r + \Delta \quad (4.3)$$

where ρ_i and ρ_r are the ideal and the residual resistivities, Δ is the deviation from Matthiessen's rule. These deviations would occur when one or both of the assumptions A and B are violated. If A is violated, Δ can have either sign depending upon which of the two sides of (4.1) is greater. But when B is violated, it can be seen from the variational principle for the resistivity that Δ would always be positive [see, e.g. Ziman (1960), pp. 285-286].

To explain the observed deviations from Matthiessen's rule, various theories have been proposed, the most notable among them being by Dube (1938), Sondheimer and Wilson (1947), Koshino (1960), Kagan and Zhernov (1966) and Damon, Mathur and Klemens (1968). The first two are based on the violation of B and the other three on that of A.

We wish to point out here a cause^{*} of the deviations from Matthiessen's rule of the type A which arises from the interference between the scattering due to the thermal vibrations of the host atoms and the excess potential due to the (thermally vibrating) impurities. Such interference terms occur because it is the matrix elements, rather than the probabilities of scattering, which are additive, and have been considered in different contexts before, e.g.,

* The results described in this Chapter are being published in Bhatia and Gupta (1969).

in Krishnan and Bhatia (1944) on the resistivity of order-disorder alloys, in neutron scattering formulations, and in Faber and Ziman (1965) on the resistivity of liquid alloys. Kagan and Zhernov (1966) have considered the interference terms in connection with the deviations from Matthiessen's rule also. However, they underestimate significantly the importance of these terms (see footnote on p. 84, and discussion following eqn. (4.19)); moreover, the formulation given here is different from theirs.

§4.2 Calculation of the Deviations from Matthiessen's Rule

From (1.17), the variational expression for the resistivity, we have

$$\rho = \frac{\Pi}{J^2}, \quad (4.3)$$

where

$$\Pi = \frac{1}{2k_B T} \int (\phi_{\vec{k}} - \phi_{\vec{k}'})^2 Q(\vec{k}, \vec{k}') d\vec{k} d\vec{k}', \quad (4.4)$$

and

$$J = e \int v_{\vec{k}} \phi_{\vec{k}} \frac{\partial f_{\vec{k}}^0}{\partial E_{\vec{k}}} d\vec{k}. \quad (4.5)$$

Recalling that $Q(\vec{k}, \vec{k}') = f_{\vec{k}}^0 (1 - f_{\vec{k}'}^0) P(\vec{k}, \vec{k}')$, and using time dependent perturbation theory, we have

$$Q(\vec{k}, \vec{k}') = \frac{2\pi}{\hbar} |\langle \vec{k}' | W | \vec{k} \rangle|^2 f_{\vec{k}}^0 (1 - f_{\vec{k}'}^0) \delta(E_{\vec{k}} - E_{\vec{k}'} + \hbar\omega),$$

where $\hbar\omega$ is the energy transferred during the scattering. Substituting for $\langle \vec{k}' | W | \vec{k} \rangle$ from (2.50), one gets

$$Q(\vec{k}, \vec{k}') = \frac{2\pi}{\hbar^2 N} f_{\vec{k}}^0 (1 - f_{\vec{k}'}^0) \Gamma(\vec{q}, \omega), \quad (4.6)$$

where $\Gamma(\vec{q}, \omega)$ is the Van Hove scattering correlation function given by

$$\Gamma(\vec{q}, \omega) = \int \frac{dt}{2\pi N} e^{-i\omega t} \left\langle \sum_{i,j=1}^N w_i(q) w_j(q) e^{-i\vec{q} \cdot \vec{r}_i(0)} e^{i\vec{q} \cdot \vec{r}_j(t)} \right\rangle, \quad (4.7)$$

where $\vec{q} = \vec{k}' - \vec{k}$, N the total number of atoms in the crystal, $\vec{r}_j(t)$ the position of the atom j at time t , $w_j(q)$ the pseudopotential matrix element of the atom j in the alloy and $\langle \dots \rangle$ denotes ensemble average. Substituting (4.6) in (4.4) and restoring the factors Ω_0 (the crystal volume), $1/4\pi^3$ and $1/8\pi^3$ which had been left understood before, we get

$$\begin{aligned} \Pi &= \frac{\Omega_0}{32\pi^5 \hbar^2 k_B T} \int (\phi_{\vec{k}} - \phi_{\vec{k}'})^2 f_{\vec{k}}^0 (1 - f_{\vec{k}'}^0) \Gamma(\vec{q}, \omega) d\vec{k} d\vec{k}' \\ &= \frac{\Omega_0}{32\pi^5 \hbar^2 k_B T} \int (\phi_{\vec{k}} - \phi_{\vec{k}'})^2 f_{\vec{k}}^0 (1 - f_{\vec{k}'}^0) \Gamma(\vec{q}, \omega) dE_{\vec{k}} dE_{\vec{k}'}, \\ &\quad \times \frac{dS_{\vec{k}}}{|\text{grad}_{\vec{k}} E|} \frac{dS_{\vec{k}'}}{|\text{grad}_{\vec{k}'} E|} \end{aligned} \quad (4.8)$$

($\Omega_0 = \Omega/N$). If $\hbar\omega \ll E_F$, the integrals $\int dS_{\vec{k}}$ and $\int dS_{\vec{k}'}$ may be taken over the Fermi surface and the integrals over

$E_{\vec{k}}$ and $E_{\vec{k}'}$, may be performed independently of the surface integrals. To evaluate the $E_{\vec{k}}$ - and $E_{\vec{k}'}$ - integrals, we write $f_{\vec{k}}^0$ and $f_{\vec{k}'}^0$, explicitly, define $\epsilon_{\vec{k}} = E_{\vec{k}} - E_F$, and use $E_{\vec{k}'} = E_{\vec{k}} + \hbar\omega$. This gives

$$\Pi = \frac{\Omega_0}{32\pi^5\hbar} \iint_{\text{F.S.}} \frac{dS_{\vec{k}}}{|\text{grad}_{\vec{k}}E|} \frac{dS_{\vec{k}'}}{|\text{grad}_{\vec{k}'}E|} (\phi_{\vec{k}} - \phi_{\vec{k}'})^2 \gamma(\vec{q}), \quad (4.9)$$

where $\gamma(\vec{q})$ is given by

$$\gamma(\vec{q}) = \frac{1}{k_B T} \int d\omega \Gamma(\vec{q}, \omega) \int \frac{d\epsilon_{\vec{k}}}{(e^{\epsilon_{\vec{k}}/k_B T} + 1)(1 + e^{-(\epsilon_{\vec{k}} + \hbar\omega)/k_B T})}.$$

The integral over $\epsilon_{\vec{k}}$ gives $\hbar\omega/(1 - e^{-\hbar\omega/k_B T})$ so that, defining $\beta = \hbar/k_B T$, we get

$$\gamma(\vec{q}) = \int \frac{\Gamma(\vec{q}, \omega) \beta \omega d\omega}{1 - e^{-\beta \omega}}. \quad (4.10)$$

Using the simplest trial function (1.20), and assuming cubic symmetry and spherical Fermi surface, from (4.3), (4.5) and (4.9), we get

$$\rho \approx \mathcal{Q} \int_0^2 \gamma_{av}(x) x^3 dx, \quad (4.11)$$

where $x = q/k_F$, $\mathcal{Q} = 3\pi(m^*)^2 \Omega_0 / (4\hbar^3 e^2 k_F^2)$, and $\gamma_{av}(x)$ is the average of $\gamma(\vec{q})$ over all directions of \vec{q} in the crystal. (We recall that k_F is the Fermi wave number and m^* the effective mass.)

Let us now make the simplifying assumptions that

(a) the alloy is of the substitutional type and that the

two types of atoms A and B in it are distributed at random and (b) A and B atoms have roughly the same volume, mass and force constants, so that the effects of local strain and of changes in vibration frequency spectrum can be ignored. Then in (4.7) we can replace $w_i w_j$ by its configurational average $\overline{w_i w_j}$ before taking the thermal average. Now

$$\overline{w_i w_j} = (\bar{w})^2 + \delta_{ij} [\overline{w^2} - (\bar{w})^2] . \quad (4.12)$$

If c is the concentration of B atoms, this gives

$$\overline{w_i w_j} = [(1-c)w_A + c w_B]^2 + \delta_{ij} c(1-c)(w_A - w_B)^2 . \quad (4.13)$$

Substituting (4.13) in (4.7) and using (4.10), we get for $\gamma(\vec{q})$ (which, as may be seen from (4.9) or (4.11), determines the resistivity), the expression

$$\gamma(\vec{q}) = [(1-c)w_A + c w_B]^2 S(\vec{q}) + c(1-c)(w_A - w_B)^2 S_{inc}(\vec{q}) , \quad (4.14)$$

where

$$S(\vec{q}) = \left[\int d\omega \beta \omega / (1 - e^{-\beta \omega}) \right] \int \frac{dt}{2\pi N} e^{-i\omega t} \sum_{i,j} e^{-i\vec{q} \cdot \vec{r}_i(0)} e^{i\vec{q} \cdot \vec{r}_j(t)} , \quad (4.15)$$

$$S_{inc}(\vec{q}) = \left[\int d\omega \beta \omega / (1 - e^{-\beta \omega}) \right] \int \frac{dt}{2\pi N} e^{-i\omega t} \sum_i e^{-i\vec{q} \cdot \vec{r}_i(0)} e^{i\vec{q} \cdot \vec{r}_i(t)} . \quad (4.16)$$

Writing $S_{inc}(\vec{q}) = 1 + \theta(\vec{q})$, we get from (4.14) for $c \ll 1$,

$$\gamma(\vec{q}) \approx w_A^2 S(\vec{q}) + c(w_A - w_B)^2 + 2w_A(w_B - w_A)cS(\vec{q}) + c(w_A - w_B)^2\theta(\vec{q}) . \quad (4.17)$$

The first term in (4.17) is responsible for the ideal resistivity ρ_i of the host metal A, the second term for the residual resistivity ρ_r , and the remaining two terms give rise to Δ . One verifies that at high temperatures ($\beta\omega \ll 1$), $S_{inc}(\vec{q})=1$ and hence $\theta(\vec{q})=0$. At low temperatures ($T \ll$ Debye temperature Θ) $\theta(\vec{q})$ gives rise to a term in the resistivity which is proportional to T^2 [see Taylor* (1964)] and can dominate over the contribution ($\propto T^5$) from the third term in (4.17). For $T > \Theta$, the third term makes the dominant contribution to Δ . This is the interference term, referred to earlier and

* Koshino (1960), referred to earlier, ascribed the deviations from Matthiessen's rule to a term similar to the last term in (4.17), but with $\theta(\vec{q})$ replaced by essentially $S(\vec{q})$ and thus wrongly estimated its importance, specially at high temperatures. The error in Koshino's work has been pointed out by Taylor (1962, 64).

we confine further discussion to it only*. Denoting its contribution to Δ by Δ' , we have for Δ' and ρ_r

$$\Delta' = 2 c \int_0^2 w_A (w_B - w_A) S_{av}(x) x^3 dx, \quad (4.18)$$

$$\rho_r = c \int_0^2 (w_A - w_B)^2 x^3 dx. \quad (4.19)$$

First we note that because of Umklapp collisions $S_{av}(x)$ is strongly peaked in the backward directions ($x \approx 2$). For example, whereas $S_{av}(0) (=nk_B T \beta_c)$, where $n=N/\Omega$ and β_c is the isothermal compressibility) $\approx 10^{-2}$, $S_{av}(2) \approx 0.4$ at 273°K for sodium; at 40°K $S_{av}(2) \approx 0.04$ [see Greene and Kohn (1965)]. Thus for $T \gtrsim \Theta$, we may expect from (4.18) and (4.19) that Δ'/ρ_r will, in general, be of the order of a few percent or more, which is of the correct order of magnitude. Also since at these temperatures $S_{av}(x) \propto T$, we have $\Delta' \propto T$, as is actually observed.

* It may be of interest to mention that the theory of Faber and Ziman (1965) for the resistivity of liquid alloys, referred to earlier, contains just this type of interference term. The formulations of Krishnan and Bhatia (1944) and of Kagan and Zhernov (1966) are such that the interference term in these works is essentially proportional to $S(0)$.

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The interesting point about the expression (4.18) is the combination $w_A(w_B - w_A)$ in which the pseudopotential matrix elements w_A and w_B occur in it. This is in contrast to the expressions for Δ given in previous works [Koshino (1960), Taylor (1964), and Damon, Mathur and Klemens (1968)] where w_A and w_B essentially occur in the combination $(w_A - w_B)^2$. A consequence of (4.18) is that Δ can be of either sign. Note that because of the factor $S_{av}(x)x^3$, the sign of Δ would largely depend on the sign of $w_A(w_B - w_A)$ in the neighbourhood of $x=2$. A rough calculation using the pseudopotential matrix elements w_{Mg} , w_{Al} obtained by Gupta (1968) for Mg in Al and vice versa show that Δ should be positive for Mg in Al and negative for the complementary alloy (Al in Mg). Measurements undertaken by Seth (1967) at our suggestion in 1965 show such a difference in sign for the complementary alloys of Al-Mg; Seth and Woods* (private communication) have also found similar results for Ag-Cd, Ag-Mg and Ag-Al alloys.

To conclude, we have shown that the expression (4.18) makes a significant contribution to Δ at high temperatures, although for numerical agreement effects of local strain, deformation of vibration spectrum due to impurities, and

* I would like to thank Mr. R.S. Seth and Professor S.B. Woods for letting us see their results prior to publication.

the anisotropy of the Fermi surface, would, in general, have to be taken into consideration.

PART III

RESISTIVITY DUE TO DISLOCATIONS

Chapter 5

INTRODUCTION AND HISTORIAL BACKGROUND

§5.1 A Brief Survey of the Experimental Work

The electrical resistance of a metal is found to change, usually increase, by a few per cent^{*} when the metal is plastically deformed. Change is also observed in other electrical quantities like thermoelectric power[†], Hall coefficient, magnetoresistivity etc. The change in electrical resistivity was first observed by Bergmann (1889) and later by Coke (1890). More systematic investigations have been reported by Tammon and Dreyer (1933), Dahl (1936), and Smart, Smit and Phillips (1941).

The association of this extra resistance, $\delta\rho$, with dislocations was first suggested by Koehler (1949). Various studies of work hardening [see, e.g., Cottrell (1953)] undertaken in the wake of the discovery in 1934

* In some cases the change in resistivity on plastic deformation is very large. Geiss and van Liempt (1927) observed a change of 50% in tungsten and 18% in molybdenum.

† This, incidentally, was the first electrical property for which a change on plastic deformation of the metal was observed [Thomson (1856)].

of the connection between dislocations and plastic crystals revealed that dislocations get multiplied during cold work. In well-annealed crystals, the dislocation density N_D is of the order of $10^6 - 10^8 \text{ cm}^{-2}$ and on cold work it increases to $10^{11} - 10^{12} \text{ cm}^{-2}$. Thus the extra resistivity $\delta\rho$ may be attributed to the increase in the dislocation density.

However, as a result of the experiments of Molenaar and Aarts (1950) and of Broom (1952), it soon became clear that there are two other defects, namely vacancies and stacking faults* which contribute to $\delta\rho$. Let us denote the various contributions to $\delta\rho$ by $\delta\rho_D$, $\delta\rho_V$ and $\delta\rho_S$, where the subscripts are self-explanatory. It is found that $\delta\rho_D$ and $\delta\rho_V$ are roughly of equal magnitude while $\delta\rho_S$ is usually small but in some cases (e.g., in noble metals and in alloys such as Cu + Zn which have low stacking fault energies), $\delta\rho_S$ is about 10 - 20% of $\delta\rho$.

* Stacking faults are produced by plastic deformation of an fcc crystal because dislocations in such a crystal may dissociate into partial dislocations separated by a ribbon of stacking faults.

Experimental estimates of the resistivity of dislocations are usually expressed as $\delta\rho_D/N_D$, which we shall denote by ρ_D . At present, it is not possible to estimate ρ_D very accurately; the results are reliable, at best, within a factor of 2. The reliability of measurements is limited primarily by the uncertainty in the estimation of the dislocation density. The uncertainty in the separation of the measured resistance into its components is another important source of error.*

In Table III we give the values of ρ_D taken from different sources. The spread between the various measurements is obvious at a glance.

* Basinski et al. (1963) have drawn attention to yet another source of error in the estimation of ρ_D , arising from the possibility of a rearrangement of the impurity ions when the crystal is plastically deformed.

Table III. Values of ρ_D in 10^{-19} ohm-cm³ for Cu and Al as reported by different workers.

Cu		Al	
ρ_D	Source	ρ_D	Source
2.3(4.2°K) [†]	Blewitt et al. (1955)	3.3 (80°K) [†]	Clarebrough et al. (1961)
3.0(80°K)	Clarebrough et al. (1961)	7 ± 2(80°K)	Cotterill(1963)
1 (4.2°K)	Basinski and Saimoto (1967)	6.4 (80°K)	Yoshida et al. (1963)
1.3(4.2°K)	Rider and Foxon (1967)	2.9±0.4(80°K)	Rider and Foxon (1966)
1.6(77°K)		1.8±0.1(4.2°K)	

[†] This indicates the temperature at which the measurement was made.

§5.2 Theory of the Dislocation Resistivity

§5.2.1 Previous Theories

The theory of the resistivity due to dislocations is an extremely controversial topic. There is a large discrepancy between the experimental and the theoretical values of ρ_D - the latter being lower by a factor of the order of 10, usually more. Even though the experimental data are not quite reliable, it is unlikely that they are

systematically in error by such a large factor. It is generally agreed that the theory needs to be improved but there is general disagreement about the source of the discrepancy. A number of possibilities have been suggested but the extent of their influence is far from clear.

Three different approaches, called the rigid ion approach, the deformation potential, and the theories based on approximate models of the core of the dislocation, have been tried for the calculation of the probability of scattering (which forms the basis of a resistivity calculation) in the presence of dislocations.

The earliest of these was the rigid ion approach which was used by Koehler (1949) in his pioneering work on the calculation of ρ_D for edge dislocations. In this approach the screening charge is assumed to move rigidly with the ions as they are displaced from their positions in the perfect lattice, and the perturbing potential is given, in the first approximation, by the product of the displacements of the ions and the gradient of the ion potential. The difficulty caused by the displacements due to a single edge dislocation being infinite at large distances, was avoided by considering a pair of edge dislocations of opposite sign.

Koehler's work suffered from two objections. The first was that to solve the Boltzmann equation, Koehler

proceeded by expanding the distribution function as a Fourier series and retaining only the first few terms; the convergence of this procedure was not investigated. To avoid this, Mackenzie and Sondheimer (1950) suggested a procedure equivalent to the use of the simplest trial function (1.20) in a variational calculation of the resistivity. The reliability of the procedure was not clear in this case also, but it is expected to be a good approximation when the resistivity produced by dislocations in a very small fraction of the total resistivity. Moreover, the method is much simpler than that employed by Koehler and has been used in several subsequent investigations of the dislocation resistivity. The second objection against Koehler's work was the displacement in the presence of a pair of edge dislocations of opposite sign, while finite everywhere, is discontinuous across the line joining the dislocations; and this invalidates the procedure for evaluating the perturbing potential. To deal with this difficulty, Landauer (1951) introduced the deformation potential approach in which the perturbation potential depends on the strain (or the deformation) which, unlike the displacements, is finite and continuous.

In the deformation potential approach the screening charge is treated in a basically different manner. Instead of requiring this charge to move rigidly with the

ions, here one permits the electrons to redistribute themselves in the strained lattice. The tendency for the electrons to redistribute themselves in the presence of the strain arises because the Fermi energy E_F depends upon the strain. If the strain is inhomogeneous, E_F varies from place to place in the crystal and electrons flow so as to make it uniform. The perturbing potential is the potential caused by the redistribution of charge. It was shown by Dexter (1952) [see also Harrison (1958a)] that this method of evaluating the perturbing potential is justified if the strains vary slowly.

The treatment of Landauer was based on the nearly free electron (NFE) approximation. This was later generalized by Hunter and Nabarro (1953). In the NFE approximation E_F , hence the perturbing potential, depends only on the dilatational strain. However the general treatment of Hunter and Nabarro showed that a shear strain also gives rise to a perturbing potential. This has an important bearing on the resistivity of screw dislocations whose strain field is one of pure shear in the approximation of the linear elastic theory.

The calculations of Hunter and Nabarro gave a value $6 \times 10^{-21} \Omega\text{-cm}^3$ for ρ_D of edge dislocations in Cu. This may be compared with the most recent experimental estimate (see Table III) of $1 \times 10^{-19} \Omega\text{-cm}^3$. The experimental value

of ρ_D is, of course, based on an estimate of the dislocation density N_D which includes both the edge and the screw dislocations, but this only makes the discrepancy more serious since the resistivity due to screw dislocations is expected to be small [Harrison (1958a)].

The calculation of Hunter and Nabarro has been criticized by Carruthers (1959) and by Seeger and Bross (1960), but the objections do not appear to be well founded [see Nabarro (1968) p. 630]. However, there is one weakness of the theory, namely the inadequacy of its treatment of the scattering due to the core of the dislocation, which had been known from the very beginning but it has not been clear what to do about it. The effect of the core had been treated only as an extrapolation of the linear strain field. This is, of course, incorrect because of the severe distortion of the lattice at the core. But a proper treatment of the core is beset with two difficulties - evaluation of the strain in the region of the core and the evaluation of the perturbing potential due to this strain (the deformation potential would not be adequate for this purpose because the strain in the core is not slowly varying).

To provide some estimate of the scattering due to the core, Harrison (1958) suggested a model, called the

hollow cylinder model, for the core of the dislocation. The model is questionable in detail but has the essential features of the core i.e., the interaction is relatively strong and is restricted to a region of atomic dimensions. Considering this cylinder to be a row of vacancies and ignoring the linear strain field altogether, Harrison found ρ_D for Cu to be $5 \times 10^{-20} \Omega\text{-cm}^3$. This is about 10 times the value obtained by Hunter and Nabarro and compares favourably with the experimental value of $1 \times 10^{-19} \Omega\text{-cm}^3$. Calculations have also been made on similar lines by Basinski et al. (1963) and Ziman (1964) with the difference that their estimate of the dislocation resistivity was based on the mean square displacement of the ions in the presence of a dislocation. Estimating the value of this mean square displacement, from plausibility arguments, to be the Burgers vector of the dislocation (\approx interatomic spacing), both Basinski et al. and Ziman obtained reasonable agreement with experiment.

§5.2.2 The Present Work

The theories discussed above are inadequate in one or both of the two important aspects of a resistivity calculation: (1), the calculation of the probability of scattering $P(\vec{k}, \vec{k}')$ and (2), the calculation of the resis-

tivity using this probability of scattering. Because of their inability to deal properly with the core, the theories of Koehler, Mackenzie and Sondheimer, Landauer and of Hunter and Nabarro are mainly inadequate in the first aspect. Their calculation of the resistivity is based on approximate methods, the reliability of which has not been tested before. On the other hand, the theories of Harrison (1958), Basinski et al. (1963) and of Ziman (1964) are mainly inadequate in the second aspect. Their estimate of $P(\vec{k}, \vec{k}')$, though still not satisfactory, is considerably improved, but their calculation of the resistivity is crude: Even the anisotropy of the dislocation resistivity has not been taken into account.

The present work was started in an effort to construct a theory satisfactory in both the aspects. The calculation of $P(\vec{k}, \vec{k}')$ has now become possible (see Chapter 2) by the development of the pseudopotential technique. In this method, we are no longer bothered by infinite displacements since what matters is the pair correlation function or the relative displacements. The manner in which the strains may vary is also not a limitation any longer. For calculating $P(\vec{k}, \vec{k}')$, all we have to know is the form factors of the ions and the structure factor.

However, the solution of the second difficulty is not quite as simple. Difficulties in this arise when we try to solve the Boltzmann equation in the presence of such a highly anisotropic object as the dislocation. One is, therefore, faced with two alternatives - either to use some approximate method for solving the Boltzmann equation or to use some simple model for the dislocation so that the Boltzmann equation may be solved exactly: We decided in favour of the latter. Treating the dislocation to be a row of weak scatterers each having a spherically symmetric potential, we have been able to obtain an exact analytical solution of the Boltzmann equation in the presence of a set of parallel dislocations. This decision was taken for several reasons. Firstly, the preliminary investigation made by Harrison shows that, though crude, the model is not far from reality and it is of interest to obtain a reliable estimate of the resistivity on its basis. Secondly, if we can extend our solution to the case where the potential due to the individual scatterers is allowed to have radial asymmetry in the plane perpendicular to the row, the model would simulate the scattering due to an exact

arrangement of the ions in an edge dislocation[†] (see figure 1). Thirdly, an exact solution, if only for a simple model, is important because it can be used as a guide to the reliability of the various approximate procedures; or, if one wants to use the variational technique, for making a more educated guess about the trial function rather than using the simplest trial function given by (1.20).

To take care of the expected deviations from Matthiessen's rule we have solved the Boltzmann equation in the presence of other mechanisms of scattering, but in order that our method applies in its present form, we require to put the restriction that the scattering due to these other mechanisms depends only on the relative orientation of \vec{k} and \vec{k}' .

Chapter 6 deals with the solution of the Boltzmann equation and Chapter 7 with the calculation of the resistivity. The resistivity due to both parallel and random dislocations is discussed. For random dislocations, an alternative to the usual method for determining the resistivity is discussed.

[†] In as much as the core a screw dislocation also has a dilatation [see e.g., Nabarro (1968) p. 617], the simple model used here provides an estimate for the resistivity due to a screw dislocation also.

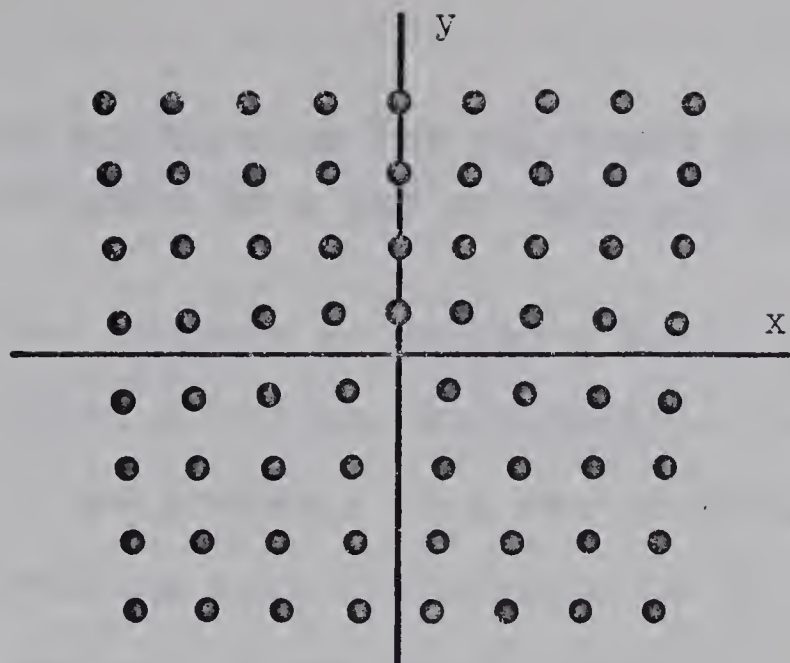


Fig. 1. A unit edge dislocation in a simple cubic lattice. The dislocation is along the z-axis and the slip direction along the x-axis.

Chapter 6

THE SOLUTION OF THE BOLTZMANN EQUATION IN THE PRESENCE OF A SET OF PARALLEL DISLOCATIONS

In this chapter we obtain a solution of the Boltzmann equation for the distribution function in a crystal in the presence of a set of parallel dislocations treating each dislocation to be a row of scatterers having a spherically symmetric potential. Along with dislocations, other mechanisms of scattering may also be present with the restriction that the scattering due to the other mechanisms depends only on the angle between \vec{k} and \vec{k}' . The energy surfaces in k -space will be assumed to be spherical.

One approach to this problem is to try to solve the integral equation (1.7) for the anisotropic relaxation time $\tau_{\vec{k}}$. For the simple case of isotropic scatterers (1.7) was solved by Bhatia (1949) but the method does not appear to be adaptable to an easy generalization.

The method we use here is based on an approach used previously by Bhatia and Moore (1961). It consists in reducing the solution of the Boltzmann equation to the solution of a difference equation, the unknowns of the difference equation being $f_{LM}(k)$, the coefficients expansion of the distribution function $f_{\vec{k}}$ in spherical harmonics. In general, this problem may be as difficult

as the original problem itself. But in our case it turns out that the solution of the difference equation can be reduced to the solution of a number of linear equations for the unknowns f_{LM} . From here f_{LM} 's can be obtained if certain quantities associated with the scattering due to the dislocations and the other mechanisms can be expanded in a finite number of Legendre polynomials. If ℓ_0 and L_0 respectively are the degrees of the highest-degree polynomial in the expansion of the relevant quantities in the dislocation scattering and the scattering due to the other mechanisms, L_0 is required to be finite so that the number of equations we have to solve is finite and ℓ_0 is required to be finite so that the coefficients of the unknowns in these equations may be calculated. Since it is reasonable to assume that in a physical problem both ℓ_0 and L_0 would be finite, the whole problem boils down to solving a finite number (usually of the order of 5) of linear equations.

In §6.1 we shall obtain the difference equation for the f_{LM} 's; the solution of that will be discussed in §6.2.

§6.1 Derivation of the Difference Equation for the f_{LM} 's

The Boltzmann equation for the distribution function is given by (1.1). Substituting for $\left[\frac{\partial f_{\vec{k}}}{\partial t} \right]_{\text{field}}$ from (1.2b)

and $\left[\frac{\partial f_{\vec{k}}}{\partial t} \right]_{\text{coll}}$ from (1.5) and recalling that the \vec{k}' -integration contains a factor $\Omega/8\pi^3$ which had been left understood, we get

$$- \frac{e}{\hbar} \vec{\epsilon} \cdot \hat{k} \frac{\partial f_{\vec{k}}^0}{\partial k} = \frac{\Omega}{8\pi^3} \int P(\vec{k}, \vec{k}') (f_{\vec{k}} - f_{\vec{k}'}) d\vec{k}' , \quad (6.1)$$

We shall assume that the probabilities of $P_1(\vec{k}, \vec{k}')$ and $P_2(\vec{k}, \vec{k}')$ of scattering due to dislocations and other mechanisms respectively are additive. Thus

$$P(\vec{k}, \vec{k}') = P_1(\vec{k}, \vec{k}') + P_2(\vec{k}, \vec{k}') , \quad (6.2)$$

in which, as mentioned before, $P_2(\vec{k}, \vec{k}')$ will be assumed to depend on $|\vec{k} - \vec{k}'|$ only.

Expanding $f_{\vec{k}}$ in terms of spherical harmonics, we have

$$f_{\vec{k}} = f_{\vec{k}}^0 + \sum'_{LM} f_{LM} Y_{LM}(\beta, \psi) , \quad (6.3)$$

where (k, β, ψ) are the spherical coordinates of \vec{k} with respect to the system of coordinates in which the polar axis is along the direction of the dislocation lines. Here the sum represents the deviation of $f_{\vec{k}}$ from $f_{\vec{k}}^0$ on the application of the electric field. The L -summation is over all positive integers and M takes all integral values from $-L$ to $+L$. The prime over the summation sign stands for the exclusion of the term $L=0$ but it will be left understood in future.

Writing a similar expansion for $f_{\vec{k}'}$, we have

$$f_{\vec{k}'} = f_k^0 + \sum_{LM} f_{LM} Y_{LM}(\alpha, \phi), \quad (6.4)$$

where $[k' (=k), \alpha, \phi]$ are the polar coordinates of \vec{k}' .

Note that the scattering being elastic, the coefficients f_{LM} and the isotropic part f^0 are the same for $f_{\vec{k}}$ and $f_{\vec{k}'}$.

Using (6.2)-(6.4) and again taking the energy surface to be spherical, equation (6.1) may be written as

$$-\frac{e}{\hbar} \vec{\epsilon} \cdot \hat{k} \frac{\partial f_k^0}{\partial k} = I_1 + I_2, \quad (6.5)$$

where

$$I_1 = \frac{\Omega}{8\pi^3} \int k'^2 P_1(k, k') \sum_{LM} f_{LM} [Y_{LM}(\beta, \psi) - Y_{LM}(\alpha, \phi)] dk' \sin\alpha d\alpha d\phi, \quad (6.6)$$

and I_2 is given by a similar integral but with P_1 replaced by P_2 .

First let us consider I_1 . We have

$$P_1(\vec{k}, \vec{k}') = \frac{2\pi}{\hbar} |M_1(\vec{k}, \vec{k}')|^2 \delta(E_k - E_{k'}), \quad (6.7)$$

where $M_1(\vec{k}, \vec{k}')$ is the scattering matrix element due to the dislocations. For one dislocation $M_1(\vec{k}, \vec{k}')$ is given by

$$M_1(\vec{k}, \vec{k}') = \frac{1}{N} w(q) \sum_{r=0}^{n-1} \exp[-ik(\cos\alpha - \cos\beta)ra],$$

so that

$$|M_1(\vec{k}, \vec{k}')|^2 = \frac{1}{N^2} [w(q)]^2 \frac{\sin^2 [\frac{1}{2} nka(\cos\alpha - \cos\beta)]}{\sin^2 [\frac{1}{2} ka(\cos\alpha - \cos\beta)]},$$

where n is the number of scatterers constituting the row, a the distance between the scatterers, $w(q)$ their form factor and N the total number of ions in the crystal. (Note that since the potential due to individual scatterers has been assumed to be spherically symmetric, w depends only on the magnitude of \vec{q} .)

If there are N_0 dislocations in the crystal, $P_1(\vec{k}, \vec{k}')$ will be given by

$$P_1(\vec{k}, \vec{k}') = \frac{2\pi}{h} \frac{N_0}{N^2} [w(q)]^2 \frac{\sin^2 [\frac{1}{2} nka(\cos\alpha - \cos\beta)]}{\sin^2 [\frac{1}{2} ka(\cos\alpha - \cos\beta)]} \delta(E_k - E_{k'}). \quad (6.8)$$

Since q depends upon k and θ ($q=2k \sin\theta/2$), where θ is the angle between \vec{k} and \vec{k}' , we can write

$$[w(q)]^2 = \sum_{\ell=0}^{\infty} c_{\ell}^{(1)}(k) P_{\ell}(\cos\theta), \quad (6.9)$$

where $P_{\ell}(\cos\theta)$ are the Legendre polynomials*. Substituting (6.8) and (6.9) in (6.6), noting that

* No confusion should arise from the use of symbol P for probabilities as well as for Legendre polynomials.

$$\int k'^2 \delta(E_k - E_{k'}) dk' = k^2 \left(\frac{dE}{dk} \right)^{-1}, \quad (6.10)$$

and using

$$P_\ell(\cos\theta) = \frac{4\pi}{2\ell+1} \sum_m Y_{\ell m}(\beta, \psi) Y_{\ell m}^*(\alpha, \phi), \quad (6.11)$$

we get

$$\begin{aligned} I_1 = & \frac{N_o \Omega_o k^2}{\pi \hbar N} \left(\frac{dE}{dk} \right)^{-1} \sum_{\ell m LM} \frac{c_\ell^{(1)}}{2\ell+1} f_{LM} Y_{\ell m}(\beta, \psi) \times \\ & \times \int Y_{\ell m}^*(\alpha, \phi) \frac{\sin^2 \left[\frac{1}{2} nka(\omega' - \omega) \right]}{\sin^2 \left[\frac{1}{2} ka(\omega' - \omega) \right]} [Y_{LM}(\beta, \psi) - Y_{LM}(\alpha, \phi)] d\omega' d\phi, \end{aligned} \quad (6.12)$$

where $\omega = \cos\beta$ and $\omega' = \cos\alpha$. Here, the integration over ω' behaves as a delta function and we get

$$\begin{aligned} I_1 = & \sum_{\ell LM} c'_\ell f_{LM} \{ Y_{LM}(\beta, \psi) [\mathcal{P}_{\ell o}(\omega)]^2 \\ & - Y_{\ell M}(\beta, \psi) \mathcal{P}_{\ell M}(\omega) \mathcal{P}_{LM}(\omega) \} \\ = & \sum_{\ell LM} c'_\ell f_{LM} Y_{LM}(\beta, \psi) \{ [\mathcal{P}_{\ell o}(\omega)]^2 - [\mathcal{P}_{\ell M}(\omega)]^2 \}, \end{aligned} \quad (6.13)$$

where

$$c'_\ell = \frac{N_o n \Omega_o k c_\ell^{(1)}}{(2\ell+1) N \hbar a} \left(\frac{dE}{dk} \right)^{-1}, \quad (6.14)$$

and \mathcal{P}_{LM} are defined by

$$Y_{LM}(\beta, \psi) = \frac{1}{\sqrt{4\pi}} \mathcal{P}_{LM}(\omega) e^{iM\psi}, \quad (6.15)$$

or, equivalently, by

$$\phi_{LM}(\omega) = N_{LM} P_L^M(\omega) , \quad (6.16)$$

where $P_L^M(\omega)$ are the associated Legendre polynomials and N_{LM} are given by

$$N_{LM} = \left[(2L + 1) \frac{(L-M)!}{(L+M)!} \right]^{\frac{1}{2}} \quad (6.17)$$

Noting that the density of dislocations N_D is equal to $(N_0 na / \Omega)$, we can write c'_ℓ in terms of N_D . This gives

$$c'_\ell = \frac{N_D \Omega_o^2 k c_\ell^{(1)}}{(2\ell+1) na^2} \left(\frac{dE}{dk} \right)^{-1} . \quad (6.18)$$

Now let us evaluate I_2 . For $P_2(\vec{k}, \vec{k}')$ we can write down an expression similar to the expression (6.7) for $P_1(\vec{k}, \vec{k}')$. But now the matrix element would depend only on the relative orientations of \vec{k} and \vec{k}' . Therefore we can write

$$\frac{\Omega}{8\pi^3} \int k'^2 P_2(|\vec{k} - \vec{k}'|) dk' = k^2 \sum_{\ell=0}^{\infty} c_\ell^{(2)}(k) P_\ell(\cos\theta) . \quad (6.19)$$

Substituting (6.19) in (6.6) and using (6.11), we get

$$\begin{aligned} I_2 &= \sum_{\ell m LM} c_\ell'' f_{LM} Y_{\ell m}(\beta, \psi) \int Y_{\ell m}^*(\alpha, \phi) [Y_{LM}(\beta, \psi) - Y_{LM}(\alpha, \phi)] d\omega' d\phi \\ &= \sum_{LM} (c_o'' - c_L'') f_{LM} Y_{LM}(\beta, \psi) , \end{aligned} \quad (6.20)$$

where

$$c_\ell'' = c_\ell^{(2)} \frac{4\pi k^2}{2\ell+1} . \quad (6.21)$$

Next we consider the left hand side of the Boltzmann equation (6.5). If we choose the z-axis along the dislocation lines (which is also the direction of the polar axis for the spherical coordinates we are using), $\vec{\epsilon} \cdot \hat{k}$ is given by

$$\vec{\epsilon} \cdot \hat{k} = \epsilon_x \sin\beta \cos\psi + \epsilon_y \sin\beta \sin\psi + \epsilon_z \cos\beta. \quad (6.22)$$

Hence

$$-\frac{e}{\hbar} \frac{\partial f^0}{\partial k} \vec{\epsilon} \cdot \hat{k} = \sum_m A_{lm} Y_{lm}(\beta, \psi), \quad (6.23)$$

where

$$A_{10} = -\frac{e}{\hbar} \frac{\partial f^0}{\partial k} \left(\frac{4\pi}{3}\right)^{1/2} \epsilon_z \quad (6.24)$$

$$A_{1,\pm 1} = -\frac{e}{\hbar} \frac{\partial f^0}{\partial k} \left(\frac{2\pi}{3}\right)^{1/2} (\epsilon_x \mp i\epsilon_y).$$

Using (6.23), (6.13) and (6.20), the Boltzmann equation (6.5) reduces to

$$\begin{aligned} & \sum_{LM} (c''_O - c''_L) f_{LM} Y_{LM}(\beta, \psi) \\ & + \sum_{\ell LM} c'_\ell f_{LM} Y_{LM}(\beta, \psi) \{[\mathcal{P}_{\ell O}(\omega)]^2 - [\mathcal{P}_{\ell M}(\omega)]^2\} \\ & = \sum_m A_{lm} Y_{lm}(\beta, \psi) \end{aligned} \quad (6.25)$$

The Difference Equation

We have thus expressed the Boltzmann equation (6.5) in a form where instead of determining $f_{\vec{k}}$ directly, we can determine its components f_{LM} . The fact that f_{LM} 's are infinite in number does not necessarily make this reformulation more difficult because firstly, many of them would be identically zero; and secondly, for determining a physical property of interest, we may not require all of the nonzero f_{LM} 's, e.g., as will be seen in the next chapter, for determining the three components of \vec{J} , hence for determining the conductivity (or resistivity) tensor, we need only three of them, namely f_{10} and $f_{1,\pm 1}$.

Now (6.25) contains all the f 's mixed together. The f 's we want may be disentangled from the rest partly by using the orthogonality of the spherical harmonics, which gives a difference equation for f_{LM} , and partly by solving the difference equation thus obtained.

To derive the difference equation for f_{LM} from (6.25) we proceed as follows:-

1. In order to be able to take advantage of the orthogonality of the spherical harmonics, we try to rewrite (6.25) in such a manner that, just as on the

RHS, each term on the LHS also is a single spherical harmonic. This may be done in two steps: First express the terms involving products of $Y_{LM}(\beta, \psi)$ and other angle dependent quantities as a series of single spherical harmonics; then, rearrange the terms to get the desired form.

Thus we write

$$\begin{aligned} (c''_O - c''_L)Y_{LM}(\beta, \psi) + \sum_{\ell} c'_{\ell} Y_{LM}(\beta, \psi) \{[\varphi_{\ell O}(\omega)]^2 - [\varphi_{\ell M}(\omega)]^2\} \\ = \sum_j c(j, L, M) Y_{L+j, M}(\beta, \psi), \end{aligned} \quad (6.26)$$

where j takes positive as well as negative values and $c(j, L, M)$ can be determined in terms of the coefficients c' and c'' . Combining (6.26) and (6.25) gives

$$\sum_{jLM} c(j, L, M) f_{LM} Y_{L+j, M}(\beta, \psi) = \sum_m A_{lm} Y_{lm}(\beta, \psi),$$

which may be rewritten as

$$\sum_{jLM} c(j, L-j, M) f_{L-j, M} Y_{LM}(\beta, \psi) = \sum_m A_{lm} Y_{lm}(\beta, \psi), \quad (6.27)$$

which is the desired form.

2. Using the orthogonality of spherical harmonics, now gives

$$\sum_j c(j, L-j, M) f_{L-j, M} = A_{lM} \delta_{Ll} \delta_{Mm}, \quad (6.28)$$

so that the RHS of (6.28) is zero unless $L=l$ and

$M=m(=0, \pm 1)$. If the number of terms in the above sum is finite, (6.28) is the required difference equation.

Note that, in general, the RHS of (6.26) will be of the form $\sum_{jM'} c(j, L, M, M') Y_{L+j, M+M'}(\beta, \psi)$, in which case the LHS of (6.28) would be $\sum_{jM'} c(j, L-j, M-M', M') \times f_{L-j, M-M'}$. Here a simpler form for (6.26) results from the fact that $Y_{LM}(\beta, \psi)$ is multiplied by terms independent of ψ . Therefore, while there is a mixing of L in the difference equation, there is no mixing of M . In a more realistic model of the dislocation, that may also be expected.

Now we proceed to evaluate $c(j, L, M)$ for the three values of $M(=0, \pm 1)$ for which the RHS of (6.28) is different from zero.

For $M=0$, we have from (6.26) that

$$\sum_j c(j, L, 0) Y_{L+j, 0}(\beta, \psi) = (c''_0 - c''_L) Y_{LM}(\beta, \psi) .$$

$$\therefore c(j, L, 0) = (c''_0 - c''_L) \delta_{j0} .$$

Combining this with (6.28) gives

$$f_{L0} = \frac{A_{10}}{c''_0 - c''_L} \delta_{L1} = \frac{A_{10}}{c''_0 - c''_1} \delta_{L1} . \quad (6.29)$$

As regards $M=\pm 1$, it is clear from (6.26) that $c(j, L, M)$ will be the same for both of these values. So let us rewrite (6.26) for $M=1$. This gives

$$\begin{aligned}
& (c''_0 - c''_L) Y_{L1}(\beta, \psi) + \sum_{\ell} c'_{\ell} Y_{L1}(\beta, \psi) \{ [\mathcal{P}_{\ell 0}(\omega)]^2 - [\mathcal{P}_{\ell 1}(\omega)]^2 \} \\
& = \sum_j c(j, L, 1) Y_{L+j, 1}(\beta, \psi) .
\end{aligned} \tag{6.30}$$

To determine $c(j, L, 1)$, we note two points: one, $\sum_{\ell} c'_{\ell} \{ [\mathcal{P}_{\ell 0}(\omega)]^2 - [\mathcal{P}_{\ell 1}(\omega)]^2 \}$ when written in powers of ω , will contain only even powers of ω ; two, ω^{2n} (n is integer) when multiplied by $P_L^1(\omega)$ gives a series of terms $P_{L \pm 2r}^1$ where r varies from $-n$ to $+n$. Thus we may write

$$\sum_{\ell} c'_{\ell} \{ [\mathcal{P}_{\ell 0}(\omega)]^2 - [\mathcal{P}_{\ell 1}(\omega)]^2 \} = a_0 + a_1 \omega^2 + \dots + a_{\ell_0} \omega^{2\ell_0} \tag{6.31}$$

and

$$\begin{aligned}
\omega^{2n} P_L^1(\omega) &= {}_n k^0(L) P_L^1(\omega) + {}_n k_1^{(2)}(L) P_{L+2}^1(\omega) \\
&+ {}_n k_2^{(2)}(L) P_{L-2}^1(\omega) + {}_n k_1^{(4)}(L) P_{L+4}^1(\omega) + {}_n k_2^{(4)}(L) P_{L-4}^1(\omega) \\
&+ \dots + {}_n k_1^{(2n)}(L) P_{L+2n}^1(\omega) + {}_n k_2^{(2n)}(L) P_{L-2n}^1(\omega) .
\end{aligned} \tag{6.32}^{\dagger}$$

ℓ_0 in (6.31) is the highest Legendre polynomial in the expansion of $[\mathcal{W}(q)]^2$ - see (6.9). In (6.32), the superscript on k denotes the magnitude of the change in L , the

[†] If $2n > L$, clearly ${}_n k^{(2r)}(L)$ will be nonzero only for $2r \leq L$.

pre-subscript is self-explanatory and the post-subscript indicates whether L has decreased or increased - 1 denotes increase, 2 denotes decrease, and no post-subscript means no change in L . It may be mentioned that the coefficients a in (6.31) and the coefficients k in (6.32) can be determined, but, as will be seen later, we will not need to determine them.

Substituting (6.32) and (6.31) in (6.30), we immediately obtain

$$c_{1,2}(2r, L, 1) = [a_r r k_{1,2}^{(2r)}(L) + a_{r+1} r+1 k_{1,2}^{(2r)}(L) + \dots + a_{\ell_0} \ell_0 k_{1,2}^{2r}(L)] \frac{N_{L1}}{N_{L+2r,1}} + (c''_0 - c''_L) \delta_{r0}, \quad (6.33)$$

where, just like k_1 and k_2 , c_1 and c_2 correspond respectively to increase and decrease in L .

Combining this with (6.29), we obtain the difference equation

$$\begin{aligned} & (c''_0 - c''_L) f_L + \\ & [a_0 + a_1 k_1^0(L) + a_2 k_2^0(L) + \dots + a_{\ell_0} \ell_0 k_2^0(L)] f_L \\ & + [a_1 k_1^{(2)}(L-2) + a_2 k_2^{(2)}(L-2) + \dots + a_{\ell_0} \ell_0 k_2^{(2)} \\ & \quad \times (L-2)] f_{L-2} \\ & + [a_1 k_2^{(2)}(L+2) + a_2 k_2^{(2)}(L+2) + \dots + a_{\ell_0} \ell_0 k_2^{(2)} \\ & \quad \times (L+2)] f_{L+2} \end{aligned}$$

$$\begin{aligned}
& + [a_2 {}_2k_1^{(4)}(L-4) + \dots + a_{\ell_0} {}_{\ell_0}k_1^{(4)}(L-4)] f_{L-4} \\
& + [a_2 {}_2k_2^{(4)}(L+4) + \dots + a_{\ell_0} {}_{\ell_0}k_2^{(4)}(L+4)] f_{L+4} + \dots + \\
& + a_{\ell_0} {}_{\ell_0}k_1^{(2\ell_0)}(L-2\ell_0) f_{L-2\ell_0} + a_{\ell_0} {}_{\ell_0}k_2^{(2\ell_0)}(L+2\ell_0) f_{L+2\ell_0} \\
& = A \delta_{L1} \quad , \quad (6.34)
\end{aligned}$$

where $f_L \equiv f_{L1} N_{L1}$ and $A = A_{11} N_{11}$.

The difference equation for $M=-1$ will be the same except that on the RHS, we will have $A_{1,-1}$ instead of A_{11} .

§6.2 Solution of the Difference Equation

The method of solving (6.34) is suggested by the relation

$$\alpha(L-2r) {}_m k_1^{(2r)}(L-2r) = \alpha(L) {}_m k_2^{(2r)}(L), \quad (6.35)$$

where $\alpha(L) = (2L+1)/[2L(L+1)]$, which is proved in Appendix II.

First we rearrange (6.34) to obtain

$$\begin{aligned}
& (c''_0 - c''_L + a_0) f_L \\
& + a_1 [{}_1k^0(L) f_L + {}_1k_1^{(2)}(L-2) f_{L-2} + {}_1k_2^{(2)}(L+2) f_{L+2}] \\
& + \dots + a_{\ell_0} [{}_{\ell_0}k^0(L) f_L + {}_{\ell_0}k_1^{(2)}(L-2) f_{L-2} + {}_{\ell_0}k_2^{(2)}(L+2) f_{L+2}
\end{aligned}$$

$$\begin{aligned}
& + \dots + {}_{\ell_0} k_1^{(2\ell_0)} (L-2\ell_0) f_{L-2\ell_0} + {}_{\ell_0} k_2^{(2\ell_0)} (L+2\ell_0) f_{L+2\ell_0}] \\
& = A \delta_{L1} \quad . \quad (6.36)
\end{aligned}$$

It is instructive next to consider the special case where

$$c_L'' = c_0'' \delta_{L0} \quad . \quad (6.37)$$

With this (6.36) becomes

$$\begin{aligned}
& (c_0'' + a_0) f_L + a_1 [{}_1 k^0(L) f_L + {}_1 k_1^{(2)} (1-2) f_{L-2} + {}_1 k_2^{(2)} (L+2) f_{L+2}] \\
& + \dots + a_{\ell_0} [{}_{\ell_0} k^0(L) f_L + {}_{\ell_0} k_1^{(2)} (L-2) f_{L-2} + {}_{\ell_0} k_2^{(2)} (L+2) f_{L+2} \\
& + \dots + {}_{\ell_0} k_1^{(2\ell_0)} (L-2\ell_0) f_{L-2\ell_0} + {}_{\ell_0} k_2^{(2\ell_0)} (L+2\ell_0) f_{L+2\ell_0}] \\
& = A \delta_{L1} \quad . \quad (6.38)
\end{aligned}$$

The solution

$$f_L = \frac{2L+1}{2L(L+1)} \frac{A}{c_0'' + a_0} \int_{-1}^{+1} \frac{P_L^1(\omega) P_1^1(\omega) d\omega}{1 + \gamma_1 \omega^2 + \gamma_2 \omega^4 + \dots + \gamma_{\ell_0} \omega^{2\ell_0}} \quad (6.39)$$

is suggested from the relation (6.35). It may easily be verified by substitution. This is done in Appendix II., where we also prove (6.35). γ_r in (6.39) stand for $a_r / (c_0'' + a_0)$.

Now we can readily see the modification that would be necessary if a larger number of c_L'' are nonzero, but if

c_L'' for L greater than, say L_0 , are zero. For this purpose, we rewrite (6.36) such that the LHS is the same as in (6.38), so that RHS would be

$$(A + c_1'' f_1) \delta_{L1} + c_3'' f_3 \delta_{L3} + \dots + c_{L_0}'' f_{L_0} \delta_{LL_0}, \quad (6.40)$$

where for obvious reasons, we have taken L_0 to be odd. Thus c_{L_0}'' is the highest nonzero coefficient.

Comparison of (6.40) with the RHS of (6.38) suggests the solution

$$\begin{aligned} f_L = & (B + \beta_1 f_1) \frac{2L+1}{2L(L+1)} \int \frac{P_L^1(\omega) P_1^1(\omega) d\omega}{1 + \gamma_1 \omega^2 + \dots + \gamma_{L_0} \omega^{2L_0}} \\ & + \beta_3 \frac{2L+1}{2L(L+1)} \int \frac{P_L^1(\omega) P_3^1(\omega) d\omega}{1 + \gamma_1 \omega^2 + \dots + \gamma_{L_0} \omega^{2L_0}} \\ & + \dots + \beta_{L_0} \frac{2L+1}{2L(L+1)} \int \frac{P_L^1(\omega) P_{L_0}^1(\omega) d\omega}{1 + \gamma_1 \omega^2 + \dots + \gamma_{L_0} \omega^{2L_0}}, \quad (6.41) \end{aligned}$$

where

$$B = \frac{A}{c_0'' + a_0} \quad \text{and} \quad \beta_r = \frac{c_r''}{c_0'' + a_0}.$$

The verification of (6.41) follows closely that of (6.39) and will not be shown explicitly.

Using (6.41) for $L=1, 3, \dots, L_0$ we get $\frac{L_0+1}{2}$ equations in as many f 's from where f_1, f_3, \dots, f_{L_0} may be obtained (and once these f 's are known, f_L for any

higher L may be evaluated from (6.41) directly. (For the purposes of electrical resistivity, of course, we need only f_1 .)

The system of linear equations we obtain is

$$\begin{aligned}
 (c_1'' I_{11} - 1)f_1 + c_3'' I_{13} f_3 + \dots + c_{L_0}'' I_{1L_0} f_{L_0} + A I_{11} &= 0 \\
 c_1'' I_{31} f_1 + (c_3'' I_{33} - 1)f_3 + \dots + c_{L_0}'' I_{3L_0} f_{L_0} + A I_{31} &= 0 \\
 &\dots \\
 c_1'' I_{L_0 1} f_1 + c_3'' I_{L_0 3} f_3 + \dots + (c_{L_0}'' I_{L_0 L_0} - 1)f_{L_0} + A I_{L_0 1} &= 0,
 \end{aligned}
 \tag{6.42}$$

where

$$\begin{aligned}
 I_{LL'} &= \frac{2L+1}{2L(L+1)} \int_{-1}^{+1} \frac{P_L^1(\omega) P_{L'}^1(\omega) d\omega}{c_0'' + a_0 + a_1 \omega^2 + \dots + a_{\ell_0} \omega^{2\ell_0}} \\
 &= \frac{2L+1}{2L(L+1)} \int_{-1}^{+1} \frac{P_L^1(\omega) P_{L'}^1(\omega) d\omega}{c_0'' + \sum_{\ell} c_{\ell}' \{ [\mathcal{P}_{\ell 0}(\omega)]^2 - [\mathcal{P}_{\ell 1}(\omega)]^2 \}}.
 \end{aligned}
 \tag{6.43}$$

(Note that $I_{LL'}$ and $I_{L'L}$ are not equal but are related by a simple constant $\frac{2L+1}{2L'+1} \frac{L'(L'+1)}{L(L+1)}$).

For f_{11} this gives (recall $f_{11} = f_1/N_{11}$, $A_{11} = A/N_{11}$)

$$\begin{aligned}
f_{11} = & -\frac{A_{11}}{\Delta} \left[I_{11} \begin{vmatrix} (c_3'' I_{33}^{-1}) \dots c_{L_0}'' I_{3L_0} \\ c_3'' I_{53} \dots c_{L_0}'' I_{5L_0} \\ c_3'' I_{L_0 3} \dots (c_{L_0}'' I_{L_0 L_0}^{-1}) \end{vmatrix} - I_{31} \begin{vmatrix} c_3'' I_{13} \dots c_{L_0}'' I_{1L_0} \\ c_3'' I_{53} \dots c_{L_0}'' I_{5L_0} \\ c_3'' I_{L_0 3} \dots (c_{L_0}'' I_{L_0 L_0}^{-1}) \end{vmatrix} \right. \\
& + \dots + (-1)^{(L_0-1)/2} I_{L_0 1} \begin{vmatrix} c_3'' I_{13} \dots c_{L_0}'' I_{1L_0} \\ \dots \dots \dots \\ c_3'' I_{L_0-1,3} \dots c_{L_0}'' I_{L_0, L_0-1} \end{vmatrix} \left. \right], \quad (6.44)
\end{aligned}$$

where

$$\Delta = \begin{vmatrix} (c_1'' I_{11} - 1) & c_3'' I_{13} & \dots & c_{L_0}'' I_{1L_0} \\ c_1'' I_{31} & (c_3'' I_{33}^{-1}) & \dots & c_{L_0}'' I_{3L_0} \\ \dots & \dots & \dots & \dots \\ c_1'' I_{L_0 1} & c_3'' I_{L_0 3} & \dots & (c_{L_0}'' I_{L_0 L_0}^{-1}) \end{vmatrix}$$

It may be noted that f_{11} (and so also f_{31} , f_{51} ) is proportional to A_{11} so that the deviation of f from f^0 is just proportional to certain combination of components of the electric field, as it must be.

The value of $f_{1,-1}$ (or of $f_{3,-1}$, $f_{5,-1}$ etc.) may be obtained from f_{11} (or from f_{31} , f_{51} etc.) by replacing A_{11} by $A_{1,-1}$.

Chapter 7

CALCULATION OF THE RESISTIVITY DUE TO DISLOCATIONS

In the last chapter we solved the Boltzmann equation for a crystal containing parallel dislocations and some other mechanisms of scattering. Here we first use these results to calculate the resistivity tensor ρ_{ij} for a metal. Then we discuss the resistivity due to random dislocations. Finally, we present some numerical estimates of the resistivity obtained from the model of the dislocations we have used.

§7.1 Resistivity Tensor for Parallel Dislocations

As discussed in Chapter 1, the evaluation of ρ_{ij} is based on determining J_i in terms of ϵ_j . \vec{J} is given by (1.9). Assuming, as before, the Fermi surface to be spherical, we get

$$\begin{aligned}\vec{J} &= \frac{e}{4\pi^3\hbar} \int f_{\vec{k}} \frac{\partial E}{\partial k} \hat{k} k^2 dk d\Omega \\ &= \frac{e}{4\pi^3\hbar} \int f_{\vec{k}} \hat{k} k^2 dE d\Omega .\end{aligned}$$

Therefore J_z would be

$$J_z = \frac{e}{4\pi^3\hbar} \int f_{\vec{k}} \cos\beta k^2 dE d\Omega .$$

Substituting for f_k from (6.4), we get

$$\begin{aligned} J_z &= \frac{e}{4\pi^3\hbar} \int [f_k^0 + \sum_{LM} f_{LM} Y_{LM}(\beta, \psi)] \left[\left(\frac{4\pi}{3}\right)^{\frac{1}{2}} Y_{10}^*(\beta, \psi) \right] k^2 d\Omega dE \\ &= \frac{e}{4\pi^3\hbar} \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \int f_{10} k^2 d\Omega dE. \end{aligned} \quad (7.1)$$

Similarly, for J_x and J_y we get

$$J_x = \frac{e}{4\pi^3\hbar} \left(\frac{2\pi}{3}\right)^{\frac{1}{2}} \int (f_{11} + f_{1,-1}) k^2 d\Omega dE, \text{ and} \quad (7.2)$$

$$J_y = \frac{e}{4\pi^3\hbar} \left(\frac{2\pi}{3}\right)^{\frac{1}{2}} \int (f_{1,-1} - f_{11}) k^2 d\Omega dE. \quad (7.3)$$

For the model of the dislocation we have used, f_{10} , f_{11} and $f_{1,-1}$ are proportional to A_{10} , A_{11} and $A_{1,-1}$ respectively because there is no mixing in M. Therefore we can write

$$f_{1M} = G_{1M}(c', c'') A_{1M}, \quad (7.4)$$

where $G_{1M}(c', c'')$ stands for $G_{1M}(c'_1, c'_2, \dots, c'_{L_0}; c''_1, \dots, c''_{L_0})$. G_{10} involves only c''_0 and c''_1 , and may be immediately obtained from (6.29); however, $G_{11}(=G_{1,-1})$ in general depends on all of these coefficients and has to be evaluated from (6.44) numerically [in some particular cases (see below) the dependence turns out to be simple].

Substituting (7.4) in (7.1 to 3), we get

$$\begin{aligned}
J_z &= \frac{e^2 \epsilon_z}{3\pi^2 \hbar^2} \int G_{10} k^2 \left(-\frac{\partial f^0}{\partial E} \right) \frac{dE}{dk} dE \\
J_x &= \frac{e^2 \epsilon_x}{3\pi^2 \hbar^2} \int G_{11} k^2 \left(-\frac{\partial f^0}{\partial E} \right) \frac{dE}{dk} dE \\
J_y &= \frac{e^2 \epsilon_y}{3\pi^2 \hbar^2} \int G_{11} k^2 \left(-\frac{\partial f^0}{\partial E} \right) \frac{dE}{dk} dE
\end{aligned} \tag{7.5}$$

Using (1.11), we get

$$J_z = \frac{e^2 \epsilon_z}{3\pi^2 \hbar^2} G_{10}(c'_F, c''_F) k_F^2 \left(\frac{\partial E}{\partial k} \right)_F, \tag{7.6}$$

where $c_F \equiv c(E_F)$. The expressions for J_x and J_y are similar except that instead of G_{10} , we have G_{11} and instead of ϵ_z we have ϵ_x for J_x and ϵ_y for J_y .

In all the three cases, J_i depends only on ϵ_i , which shows that the axes we have used are principal axes. The three principal resistivities are

$$\rho_{zz} = \frac{3\pi^2 \hbar^2}{e^2 k_F^2 G_{10}(c'_F, c''_F)} \left(\frac{dE}{dk} \right)_F^{-1}, \tag{7.7}$$

$$\rho_{xx} = \rho_{yy} = \frac{3\pi^2 \hbar^2}{e^2 k_F^2 G_{11}(c'_F, c''_F)} \left(\frac{dE}{dk} \right)_F^{-1}, \tag{7.8}$$

Note that since $G_{10} = (c''_0 - c''_1)^{-1}$, the value of ρ_{zz} is the same as in the absence of the dislocations, which is to be expected since a dislocation does not affect the periodicity of the lattice parallel to itself.

Furthermore, for the model of the dislocation we are using, when referring to the principal axes, there are only two independent components of ρ_{ij} .

For $\Delta\rho_D$, (7.7) and (7.8) give

$$(\Delta\rho_D)_3 = 0, \quad (\Delta\rho_D)_{1,2} = \frac{3\pi^2 \hbar^2}{e^2 k_F^2} \left(\frac{dE}{dk}\right)_F^{-1} D, \quad (7.9)$$

$$\text{where } D = [1/G_{11}(c', c'') - (c''_0 - c''_1)] . \quad (7.10)$$

Here the subscript F is left understood in the c's. It should be noticed that since $c' \propto k$, $c'' \propto k^2$, the resistivity due to the other mechanisms (which depends only on c'') depends upon energy in a different manner than the resistivity of dislocations (which involves both c' and c''). Therefore, the effect of dislocations on thermoelectric power which is proportional to $d \ln \rho / dE$, could be very different from that on the resistivity.

In general, this is about as far as one can go analytically. Now we discuss a few particular cases of interest.

1. $c'_\ell = \delta_{\ell 0}$ (i.e. the scatterers constituting the dislocation scatter isotropically): In this case, D becomes a_0 which is equal to c'_0 when other c'_ℓ are zero. This is the same result as obtained by Bhatia (1949) with the difference that to show this result, we have not made any assumption regarding the coefficients c'' while Bhatia assumed $c''_L = c''_0 \delta_{L0}$.

2. $(c''_0 + a_0) \gg c'_\ell$ for $\ell=1,2,\dots,\ell_0$: In this case we get

$$D \approx a_0 + \frac{3}{4} \int [P_1^1(\omega)]^2 (a_1 \omega^2 + a_2 \omega^4 + \dots + a_{\ell_0} \omega^{2\ell_0}) d\omega, \quad (7.11)$$

where the correction terms are of order

$\frac{a_\ell}{c''_0 + a_0}$ ($\ell = 1, 2, \dots, \ell_0$) and depend upon, apart from

c''_0 , on c''_1 and c''_3 also. These correction terms represent the deviations from Matthiessen's rule. (In the case 1 above, there are no deviations.) Note that the deviations referred to here are of the type Δ_B (see Chapter 4), since in this theory we have taken Δ_A to be zero (see Chapter 6).

Using (6.31), we get from here

$$D = \frac{3}{4} \sum_{\ell} c'_\ell \int [P_1^1(\omega)]^2 \{ [P_{\ell 0}(\omega)]^2 - [P_{\ell 1}(\omega)]^2 \} . \quad (7.12)$$

This can be easily evaluated and it gives

$$\begin{aligned} D &= -3 \sum_{\ell} c'_\ell / (2\ell-1)(2\ell+3) \\ &= c'_0 - 3 \sum_{\ell} \frac{c'_\ell}{(2\ell-1)(2\ell+3)} , \end{aligned} \quad (7.13)^\dagger$$

[†] The expression on the RHS of (7.13) is nonnegative, as it must be. This can be seen by using the definition of c'_ℓ (eqn. 6.18) and by noting that $\sum_{\ell} \frac{P_\ell(\cos \theta)}{(2\ell-1)(2\ell+3)} \leq \frac{1}{3}$,

since $\sum_{\ell} \frac{1}{(2\ell-1)(2\ell+3)} = \frac{1}{3}$ and $[P_\ell(\cos \theta)] \leq 1$.

where prime over the summation sign denotes that $l=0$ is to be excluded.

This approximation essentially corresponds to that used by Mackenzie and Sondheimer to calculate the resistivity for their model of the dislocation (see Chapter 5). Also, as may be readily verified, one would obtain for ρ the expression (7.9) with D given by (7.13) if one uses the variational expression for the resistivity with the simplest trial function.

Numerical values of resistivities with and without using the approximation (2) above are presented in §7.3.

§7.2 Resistivity of Randomly Oriented Dislocations

The problem of the resistivity of random dislocations is not as simple as it may seem at first sight. There appear to be two possible ways of proceeding. One is to take the ensemble average of the resistivity such that each member of the ensemble contains parallel dislocations of density equal to the density of random dislocations in the crystal the resistivity of which we wish to determine, but the direction of the dislocations in the various members of the ensemble being random. The other method is to determine $f_{\vec{k}}$, hence the current density

and the resistivity, in the given crystal by taking the dislocations to be random at the outset.

All the theories we are aware of, use the first method - without even mentioning the second. It appears to us that both the methods are correct but they apply under different experimental situations. The most appropriate criterion for determining which of the methods would apply in a given situation, seems to be the relative value of the mean free path Λ of the electrons and the mean distance $d(=N_D^{-1/2})$ between the dislocations. If $\Lambda \ll d$, as is the case at room temperature when the dislocation density is low ($N_D \sim 10^8 \text{ cm}^{-2}$), the electrons see the dislocations of various orientations individually so that one should use the first method. However, if $\Lambda \gg d$, as is the case at low temperatures for a relatively pure sample, the second method would apply. Indeed there are situations ($\Lambda \sim d$) intermediate between these two extremes when neither of the two methods would be strictly applicable. For the intermediate case, it is not clear what one should do. The two limiting cases will be discussed below.

First Method ($\Lambda \ll d$)

The resistivity in the direction of the flow of the current for each member of the ensemble is $\vec{j} \cdot \vec{\epsilon} / j^2$.

Therefore the resistivity $\Delta\rho_D^0$ due to disordered dislocations is given by

$$\Delta\rho_D^0 = \left\langle \frac{\vec{J} \cdot \vec{\epsilon}}{J^2} \right\rangle ,$$

where $\langle \rangle$ denotes ensemble average. $\vec{J} \cdot \vec{\epsilon} / J^2$ is given by

$$\begin{aligned} \frac{\vec{J} \cdot \vec{\epsilon}}{J^2} &= \frac{J_z^2}{J^2} \frac{\epsilon_z}{J_z} + \frac{J_x^2 + J_y^2}{J^2} \frac{\epsilon_y}{J_y} \\ &= \frac{\epsilon_z}{J_z} \cos^2 \mu + \frac{\epsilon_y}{J_y} \sin^2 \mu \quad \left(\because \frac{J_x}{\epsilon_x} = \frac{J_y}{\epsilon_y} \right) , \end{aligned}$$

where μ is the angle between \vec{J} and the z-axis (or the dislocation line). This gives

$$\Delta\rho_D^0 = \frac{1}{3} (\Delta\rho_D)_3 + \frac{2}{3} (\Delta\rho_D)_1 ,$$

which is the familiar result [see, e.g., Wilson (1953) p. 197] for the mean resistivity when there is an axis of symmetry for the resistivity. (In this case the axis of symmetry is the direction of the dislocation for each member of the ensemble.) Using (7.9), this gives

$$\Delta\rho_D^0 = \frac{2\pi^2 \hbar^2}{e^2 k_F^2} \left(\frac{dE}{dk} \right)_F^{-1} D . \quad (7.14)$$

Second Method ($\Lambda \gg d$)

Let $P^0(\vec{k}, \vec{k}')$ be the probability of scattering due to random dislocations whose total number in the crystal is N_0 . From (6.8) we see that the contribution to $P^0(\vec{k}, \vec{k}')$ from dislocations lying between δ and $\delta+d\delta$, and

χ and $\chi+d\chi$, where δ and χ are the polar and the azimuthal angles with \vec{q} as the polar axis, we get from (6.8)

$$dP^0(\vec{k}, \vec{k}') = \frac{2MN_0}{\hbar N^2} [w(q)]^2 \delta(E_k - E_{k'}) \frac{\sin^2(\frac{1}{2}nqa \cos\delta)}{\sin^2(\frac{1}{2}qa \cos\delta)} \times \sin\delta d\delta d\chi, \quad (7.15)$$

or noting that $k(\cos\alpha - \cos\beta) = q \cos\delta$. This gives

$$P^0(\vec{k}, \vec{k}') = \frac{2\pi N_0}{\hbar N^2} \cdot \frac{n\pi}{aq} [w(q)]^2 \delta(E_k - E_{k'}) . \quad (7.16)$$

The result for the resistivity is now obtained either from (1.16) or directly by comparison with the resistivity given by $P_2(\vec{k}, \vec{k}')$ which, like $P^0(\vec{k}, \vec{k}')$, depends only on the magnitude of \vec{q} . We get

$$\begin{aligned} \rho_D^0 &= \frac{3\pi^2 (m^*)^2 \Omega_0}{4e^2 \hbar^2 k_F^3} \frac{N_0 n}{Na} \int_0^2 [w(x)]^2 x^2 dx \\ &= \frac{3\pi^2 (m^*)^2 \Omega_0^2 N_D}{4e^2 \hbar^3 k_F^3 a^2} \int_0^2 [w(x)]^2 x^2 dx, \end{aligned} \quad (7.17)$$

where $x = q/k_F$. Note that because of the factor $\frac{1}{q}$ in the expression (7.16) for $P^0(\vec{k}, \vec{k}')$, $[w(x)]^2$ in the expression for ρ_D^0 is weighted with x^2 rather than the usual weight factor x^3 .

In order to be able to compare it with ρ_D^0 given by (7.14), we rewrite this as

$$\rho_D^0 = \frac{3\pi^2 n^2}{e^2 k_F^2} \left(\frac{dE}{dk}\right)_F^{-1} (A_0 - A_1), \quad (7.18)$$

where

$$A_\ell = \frac{N_D \Omega_o^2 k_F^2}{2\pi a^2} \left(\frac{dE}{dk}\right)_F^{-1} \int w(x) P_\ell \left(1 - \frac{x^2}{2}\right) dx. \quad (7.19)$$

Two important differences between ρ_D^0 obtained by the two methods we have used, may be noted:-

1) Since in the first method, ρ_D^0 is obtained by averaging the corresponding result for parallel dislocations, there are deviations from Matthiessen's rule for random dislocations just as for parallel dislocations. However, in the second method ρ_D^0 is obtained from $P^0(\vec{k}, \vec{k}')$ which, like $P_2(\vec{k}, \vec{k}')$, depends only on $|\vec{q}|$. Therefore, in this there are no deviations from Matthiessen's rule (other assumptions being the same).

2) If we rewrite the expression (6.18) for c'_ℓ as [using (6.9)]

$$c'_\ell = \frac{N_D \Omega_o^2 k_F^2}{2\pi a^2} \left(\frac{dE}{dk}\right)_F^{-1} \int x [w(x)]^2 P_\ell \left(1 - \frac{x^2}{2}\right) dx, \quad (7.20)$$

we note that c'_ℓ and A_ℓ , occurring in the first and the second methods respectively, are of the same form but are weighted differently with x . Moreover, while the first method involves all the (nonzero) c'_ℓ , the second method involves only the first two A_ℓ .

§7.3 Numerical Results and their Discussion

The object of the numerical calculations was to make a systematic investigation of ρ_D for the model used. For parallel dislocations we have investigated the effect on $\rho_1 [= (\delta\rho_D)_1/N_D]$ of other mechanisms - the manner in which ρ_1 changes with the nature of these other mechanisms and with the relative value of their resistivity ρ_I and the dislocation resistivity $(\delta\rho_D)_1$ - and thus estimate the deviations from Matthiessen's rule. As regards random dislocations, their resistivity ρ_D^0 in the first method can be determined from ρ_1 itself and would, of course, depend on the type of the external mechanism present and on $\rho_I/\delta\rho_D^0$. We have also calculated ρ_D^0 by the second method in order to compare the results of the two methods. The metal chosen for this study was Al. This choice was made, on the one hand, because of the reliability with which scattering from an Al^{+3} ion in the metal can be determined from the effective potential theory and, on the other, because of the extensive experimental study which has been made on the dislocations in this metal. Just as done by Harrison (1958), the scatterers constituting the dislocations were taken to be vacancies. The other mechanisms in the presence of which the resistivity due to dislocations was investigated, were taken to be

impurities. For simplicity and because of the lack of information on the structure factor in solids, thermal scattering was not included. The impurities we tried were Mg, Zn and Cd whose form factors in Al (host) were calculated in Chapter 3.

For carrying out the numerical calculations for parallel dislocations, it is convenient to work with integrals I'_ℓ and I''_ℓ defined by

$$I'_\ell = \int_0^2 x [w(x)]^2 P_\ell(1 - \frac{x^2}{2}) dx \quad (7.21)$$

$$I''_\ell = \int_0^2 x [\Delta w(x)]^2 P_\ell(1 - \frac{x^2}{2}) dx ,$$

which occur in c'_ℓ and c''_ℓ respectively rather than working directly with the coefficients. Here w is the form factor for Al and Δw , the difference in the form factors of Al and the impurity ion in Al. From I'_ℓ and I''_ℓ , ρ_1 can be determined from (7.9) by noting with the help of (7.10) and (6.44) that

$$D(c'_\ell, c''_\ell) = \alpha D\left(\frac{c'_\ell}{\alpha}, \frac{c''_\ell}{\alpha}\right) \quad (7.22)$$

(α independent of ℓ), so that if α and β are taken to be equal to c'_ℓ/I'_ℓ and c''_ℓ/I''_ℓ respectively and γ equals β/α , we get

$$D(c'_\ell, c''_\ell) = \alpha D(I'_\ell, \gamma I''_\ell) . \quad (7.23)$$

Note that γ determines the relative value of the resistivities due to dislocations and impurities: $\rho_I/\delta\rho_D \approx \gamma I''_O/I'_O$. Thus if we determine $D(I'_\ell, \gamma I''_\ell)$ for various values of γ , (7.23) combined with (7.9) gives ρ_1 for various values of $\rho_I/\delta\rho_D$. Writing ρ_1 explicitly, we have

$$\begin{aligned} \rho_1 &= \frac{3\pi^2 \hbar}{2e^2 k_F} \left(\frac{dE}{dk} \right)_F^{-2} \frac{\Omega_0^2}{a^2} D(I'_\ell, \gamma I''_\ell) \\ &= \frac{3\pi^2 (m^*)^2}{2e^2 \hbar^3} \frac{\Omega_0^2}{k_F^3 a^2} D(I'_\ell, \gamma I''_\ell) . \end{aligned} \quad (7.24)$$

$D(I'_\ell, \gamma I''_\ell)$ for different values of γ was calculated on the IBM 360/67. The number of integrals I'_ℓ we used was 6 and that of I''_ℓ was 10. The results for various values of $R \equiv \gamma I''_O/I'_O$ for the three impurities are shown in Table IV. The expression (7.13) which, we recall, corresponds to the limit $R \rightarrow \infty$, gives $D=0.0552$.

It is clear from Table IV that D increases progressively with R so that ρ_1 increases as more and more impurities are added. The two limiting values of ρ_1 are 0.72×10^{-19} and $1.0 \times 10^{-19} \Omega \text{ cm}^3$. The increase in ρ_1 with R has a simple explanation on the basis of the variational principle. The effect of adding the impurities is that the correct variational function $\phi_{\vec{k}}$ becomes a mixture of $\phi_{\vec{k}}^{\text{dis}}$ and $\phi_{\vec{k}}^{\text{imp}}$, where the superscripts are

Table IV. Values of $D(I'_\ell, \gamma I''_\ell)$ for various values of R for dislocations in Al with Mg, Zn and Cd as impurities. Here $R = I''_0/I'_0 \approx \rho_I/\delta\rho_D$ where ρ_I is resistivity due to impurities and $\delta\rho_D$, that due to dislocations.

$R \times (1.64)^{-1}$	D in ryd ²		
	Mg	Zn	Cd
0.0	0.0401	0.0401	0.0401
1.0	0.0468	0.0462	0.0472
2.0	0.0492	0.0486	0.0495
3.0	0.0504	0.0499	0.0507
4.0	0.0512	0.0507	0.0514
6.0	0.0522	0.0518	0.0523
8.0	0.0527	0.0524	0.0529
10.0	0.0531	0.0528	0.0532
12.0	0.0533	0.0531	0.0534
16.0	0.0537	0.0535	0.0538
20.0	0.0539	0.0538	0.0540

self-explanatory. This gives rise to deviations from Matthiessen's rule, which are positive in sign (see §4.1), and hence the increase in ρ_1 . (The upper limit of ρ_1 , of course, corresponds to the use of the trial function ϕ_k^{imp} .)

As regards the resistivity ρ_D^0 of random dislocations, its value in the first method is just $\frac{2}{3} \rho_1$

so that in the two limits $R \rightarrow 0$ and $R \rightarrow \infty$, ρ_D^0 is 0.48×10^{-19} and $0.66 \times 10^{-19} \Omega \text{ cm}^3$. These may be compared (see Table III) with the most recent experimental value $1.8 \Omega \text{ cm}^3$ given by Rider and Foxon (1966). Considering the crudeness of the model of the dislocation used in the theory, the agreement with experiment is satisfactory.

We have also obtained ρ_D^0 by the second method and it was found to be $0.66 \times 10^{-19} \Omega \text{ cm}^3$. This happens to be the same as ρ_D^0 of the first method for $R \rightarrow \infty$. This, of course, must be accidental because as is clear from (7.14), [with D given by (7.13)] and (7.17), the two expressions for ρ_D^0 are quite different—even for $R \rightarrow \infty$.

§8.4 Summary and Conclusions

Using a simple model of the dislocation, where it is treated to be a row of weak scatterers with a spherically symmetric potential, we have made a systematic investigation of the resistivity due to parallel and randomly oriented dislocations in the presence of other mechanisms of scattering. By obtaining an exact solution of the Boltzmann equation for parallel dislocations, we find that on account of the deviations from Matthiessen's rule, the apparent resistivity of dislocations increases as the scattering due to the other mechanisms becomes larger and larger compared with that due to dislocations.

Numerical estimates made on dislocations in Al, taking the scatterers to be vacancies, show that the two limiting values ($R \rightarrow 0$ and $R \rightarrow \infty$, where $R = \rho_I / \delta \rho_D$) of the component of the resistivity tensor perpendicular to the dislocations differ by 30%.

As regards numerical values, the calculated resistivity ρ_D^0 of disordered dislocations, agrees with experiment sufficiently well to encourage further investigations along the same lines. In particular, a repetition of the calculations presented here using better estimates of the scattering due to the core region of the dislocation would be desirable.

On the experimental side, it would be of interest to have more information on the deviations from Matthiessen's rule as a function of temperature so that one has a better idea as to which of the two methods of averaging (see §7.2) is more appropriate in a given temperature region. This will enable one to make with some confidence estimates of anisotropy in the resistivity of a sample where dislocations are only partially aligned. There is some experimental evidence for anisotropy but in the present state of the theory a comparison is not very meaningful.

Appendix I

Evaluation of the Integral $I(q)$ occurring in Nonlocal Screening

From (2.88), $I(q)$ is given by

$$I(q) = P \int \frac{d\vec{k}(\vec{k}+\vec{q}|w^R|\vec{k})}{k^2 - |\vec{k}+\vec{q}|^2}, \quad (I.1)$$

where P denotes the principal value (henceforth, we shall leave out P , but it will be understood that we are interested in the principal value of the integral).

Two methods are available for evaluating $I(q)$; one is due to Harrison (1966) and the other due to Animalu (1965a). Below we shall discuss both of them.

Harrison's Method

Let us choose a cylindrical set of coordinates with z -axis along \vec{q} . Let the coordinates of \vec{k} be $(k_F \rho, \phi, k_F z)$. (ρ and z have been defined in this manner to make them dimensionless.) Now the various quantities $k, |\vec{k}+\vec{q}|$ and $\cos\theta$ occurring in $(\vec{k}+\vec{q}|w^R|\vec{k})$ can be expressed in terms of q, z and ρ as below:-

$$k = k_F \sqrt{z^2 + \rho^2}$$

$$|\vec{k}+\vec{q}| = k_F \sqrt{(z+q/k_F)^2 + \rho^2} \quad (I.2)$$

$$\cos\theta = \frac{k^2 + |\vec{k}+\vec{q}|^2 - q^2}{2k|\vec{k}+\vec{q}|} = \frac{k^2 + k_F q z}{k|\vec{k}+\vec{q}|}.$$

Then

$$(\vec{k}+\vec{q} | w^R | \vec{k}) = w^R(q, z, \rho) . \quad (I.3)$$

Substituting (I.3) and the first two of (I.2) in (I.1)

we get

$$I(q) = \frac{k_F^2}{q} \int_{-1}^{+1} \frac{dz}{q/k_F + 2z} \int_0^{1-z^2} w^R(q, z, y) dy , \quad (I.4)$$

where

$$y = \rho^2 . \quad (I.5)$$

The integration over y can be done straightforwardly. But in the z -integration we come across a singularity at $z = -q/2k_F$ if $q \leq 2k_F$. Harrison's method consists in making a polynomial expansion in $(z - q/2k_F)$ of the remaining factor $\int_0^{1-z^2} dy w^R(q, z, y)$ in the region of the singularity and integrating each term through the singularity exactly.

In detail the various steps are as follows:-

1. For a given q , evaluate $Y = \int_0^{1-z^2} dy w^R(q, z, y)$ for various values of z in the interval -1 to $+1$.
2. Split the integral $I(q)$ into three parts

$$J(q) = \int_{-1}^{-q/2k_F - \epsilon} \frac{dz Y(z)}{-q/2k_F + z} + \int_{-q/2k_F + \epsilon}^1 \frac{dz Y(z)}{-q/2k_F + z} \quad (I.6)$$

$$+ \int_{-q/2k_F - \epsilon}^{-q/2k_F + \epsilon} \frac{dz Y(z)}{-q/2k_F + z} .$$

3. If we choose ϵ to be sufficiently large that $1/\epsilon$ can be handled conveniently by the computer, the first two terms in (I.6) can be easily evaluated. To evaluate the third, we express Y as

$$Y = a + bz' + cz'^2 + dz'^3 + \dots, \quad (\text{I.7})$$

where

$$z' = z - q/2k_F. \quad (\text{I.8})$$

Then the last term in (I.6) becomes

$$\int_{-\epsilon}^{\epsilon} \frac{dz'}{z'} (a + bz' + dz'^2 + dz'^3 + \dots),$$

which is equal to $2\epsilon(b + d\epsilon^2/3 + \dots)$.

Animalu's Method

In Harrison's method we circumvented the difficulty of integrating through the singularity by expressing the integrand as a polynomial around the singularity and then integrating analytically. In Animalu's method one evaluates the integral $I(q)$ by the Gaussian 6-point formula and tries to pick up the points symmetrically about the singularity. The result would be the required principal value.

Let (k, α, ϕ) be the spherical polar coordinates of \vec{k} with respect to the system of coordinates whose z -axis is along \vec{q} . Now since $|\vec{k} + \vec{q}|$ and $\cos\theta$ occurring in

$(\vec{k}+\vec{q}|w^R|\vec{k})$ can be expressed in terms of k , q and ω , where ω stands for $\cos\alpha$, from (I.1) we get

$$I(q) = - \frac{2\pi}{q} \int_{-1}^{+1} d\omega \int_0^{k_F} dk \frac{k^2 w^R(k, q, \omega)}{2k\omega + q} . \quad (I.9)$$

The denominator in (I.9) vanishes on the hyperbola

$$2k\omega + q = 0 , \quad (I.10)$$

so that in the Gaussian formula the points cannot be picked up symmetrically about the singularity with k and ω as the variables of integrations. If we make the substitution

$$y = k \quad (I.11)$$

$$x = 2k\omega + q ,$$

The points A, B, C, D, E, F of Fig. 2(a) go over to A', B', C', D', E', F' of Fig. 2(b). Thus the new line of singularity is a straight line and this makes it possible to pick up the points symmetrically about the singularity.

The Jacobian of the transformation (I.11) is

$$J = \left| \frac{\partial(\omega, k)}{\partial(x, y)} \right| = \frac{1}{2y} , \quad (I.12)$$

so that (I.9) becomes

$$I(q) = - \frac{\pi}{q} \iint dx dy \frac{y \omega^R(q, x, y)}{x} \quad (I.13)$$

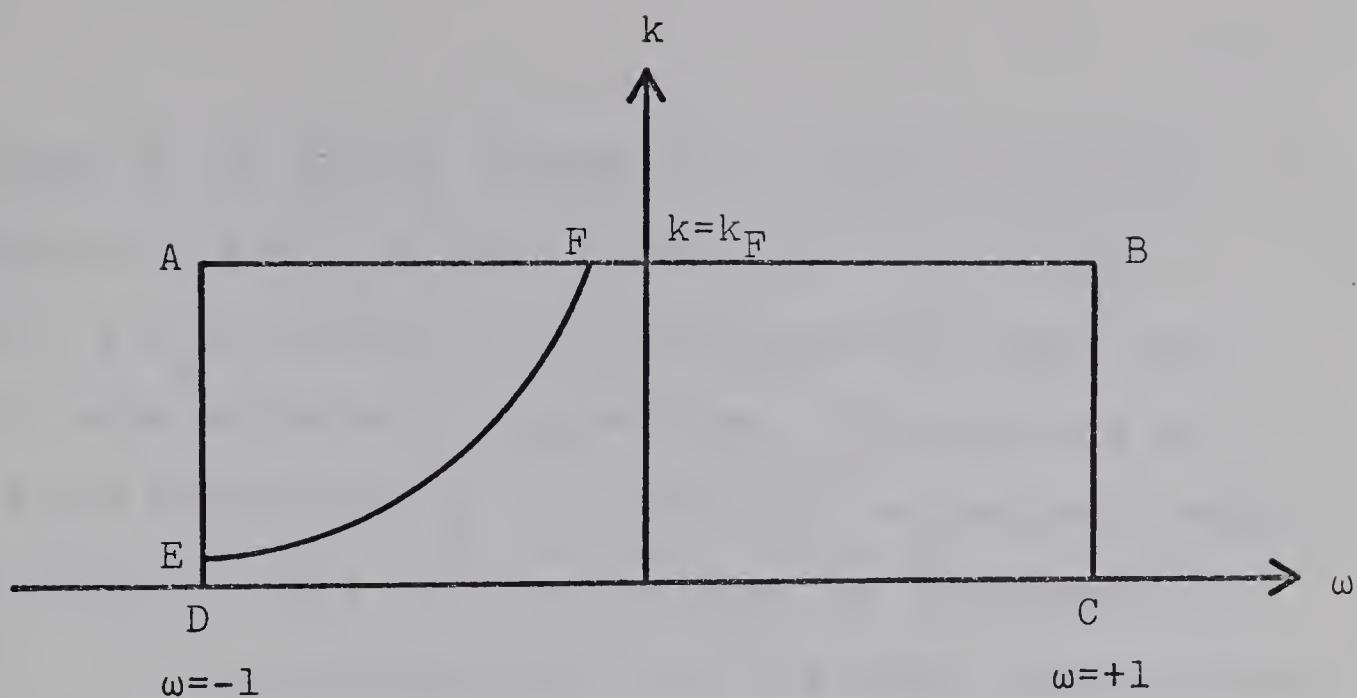


Fig. 2(a)

The plot of (I.10) for $q < k_F$.

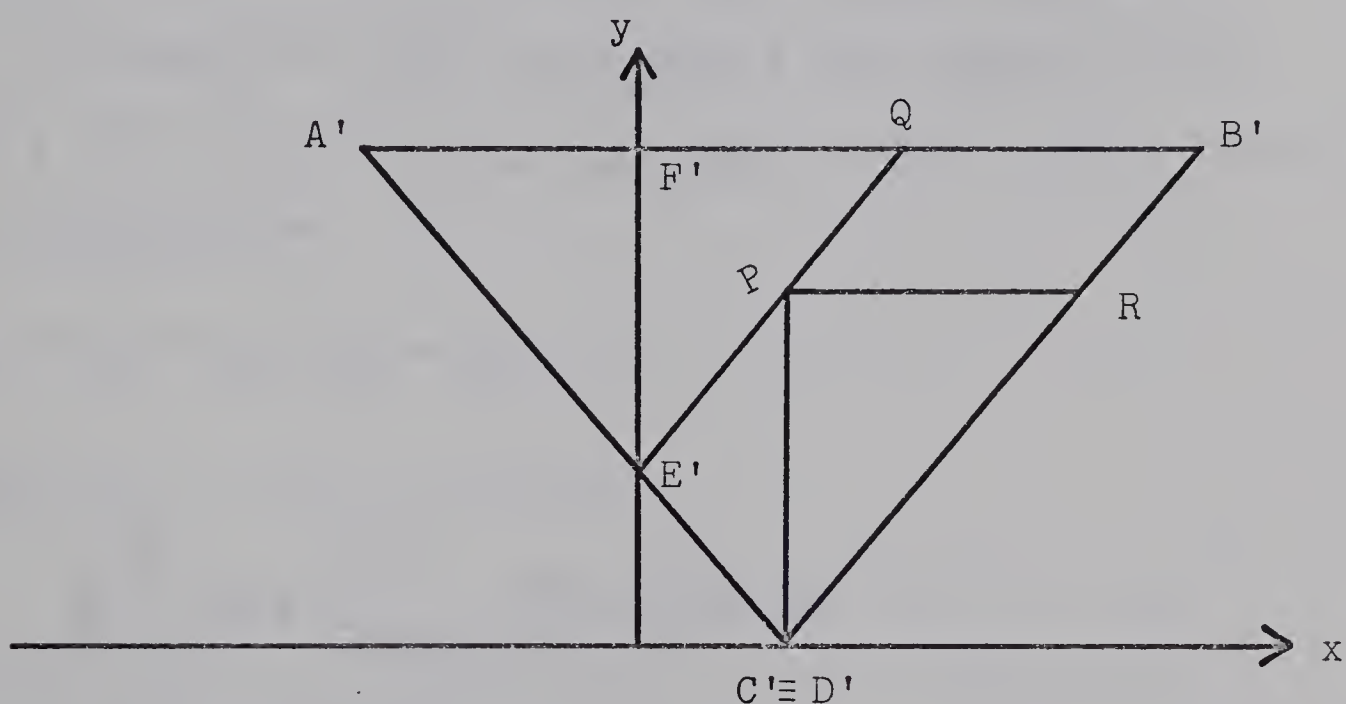


Fig. 2(b)

Remapping of the points A, B, C, D, E, F of Fig.2(a) with the transformation (I.11). The line $E'Q$ is drawn such that $A'F' = F'Q$. The points P and R on $E'Q$ and $C'B'$ respectively are such that $E'C' = E'P$ and $PQ = RB'$.

To pick up the points symmetrically about the line singularity $E'F'$, we draw a line $E'Q$. If in the region $A'E'Q$ we perform the x -integration first, we shall have achieved our objective. To take care of the point singularity E' we take $E'C'P$ as another region of integration but here we perform the y -integration first. The remaining domain is free from singularities but for convenience of choosing the limits we divide it into two parts by a line PR . In $C'PR$ and $RB'QP$ the order of integration is immaterial. Supposing we do the x -integration first, and denote the regions $A'E'Q$, $E'C'P$, $C'PR$ and $RB'QP$ by 1, 2, 3 and 4 respectively, (I.13) may be written as

$$I(q) = I_1 + I_2 + I_3 + I_4,$$

where

$$I_1 = -\frac{\pi}{q} \int_{q/2}^{k_F} y dy \int_{-(2y-q)}^{2y-q} \frac{dx}{x} \omega^R(q, x, y)$$

$$I_2 = -\frac{\pi}{q} \int_0^q \frac{dx}{x} \int_{(q-x)/2}^{(q+x)/2} y \omega^R(q, x, y) dy$$

$$I_3 = -\frac{\pi}{q} \int_0^q y dy \int_q^{q+2y} \frac{dx}{x} \omega^R(q, x, y)$$

$$I_4 = -\frac{\pi}{q} \int_q^{k_F} y dy \int_{2y-q}^{2y+q} \frac{dx}{x} \omega^R(q, x, y) .$$

Note that in Fig. 2 we have taken $q < k_F$. The discussion of the case $k_F < q \leq 2k_F$ is exactly similar. In fact as long as correct order of integrations is left, the computer deals with both of these cases in one go. The case of q greater than $2k_F$ does not present any trouble because then, the singularity lies outside the region of integrations and the whole domain can be included in one step. However, it may be pointed out that for $q > 2k_F$, though the singularity lies outside the domain of integrations, it affects the accuracy somewhat because the points in the Gaussian formula are not symmetrical about the singularity. The effect on the accuracy is greater the closer is the singularity to the region of integrations. Thus, for larger values of $(q-2k_F)$, the accuracy is better.

Comparison of the Two Methods

We have tried both the methods and find that Animalu's method is much easier to use. However, it may be added that the accuracy of the two methods is of the same order.

Appendix II

Proof of the Identity (6.35)

(6.35) is readily proved by multiplying (6.32) by $P_{L+2r}^1(\omega)$ and by $P_{L-2r}^1(\omega)$, and using

$$\int_{-1}^{+1} P_L^1(\omega) P_{L'}^1(\omega) d\omega = \frac{1}{\alpha(L)} \delta_{LL'}, \quad ,$$

where, as in the text, $\alpha(L) = (2L+1)/[2L(L+1)]$. This gives

$$n_{k_1}^{(2r)}(L) = \alpha(L+2r) \int_{-1}^{+1} \omega^{2n} P_L^1(\omega) P_{L+2r}^1(\omega) d\omega, \quad (\text{II.1})$$

and

$$n_{k_2}^{(2r)}(L) = \alpha(L-2r) \int_{-1}^{+1} \omega^{2n} P_L^1(\omega) P_{L-2r}^1(\omega) d\omega. \quad (\text{II.2})$$

Changing L to $(L-2r)$ in (II.1) gives

$$n_{k_1}^{(2r)}(L-2r) = \alpha(L) \int_{-1}^{+1} \omega^{2n} P_{L-2r}^1(\omega) P_L^1(\omega) d\omega. \quad (\text{II.3})$$

Substituting for the integral in (II.3) from (II.2), we get

$$\alpha(L-2r) n_{k_1}^{(2r)}(L-2r) = \alpha(L) n_{k_2}^{(2r)}(L), \quad (\text{II.4})$$

which is the identity (6.35), we wanted to prove.

To Verify that (6.39) is a Solution of (6.38)

We recall that (6.38) and (6.39) give

$$\begin{aligned}
 & (c''_0 + a_0)f_L + a_1 [{}_1k^0(L)f_{L+1}{}_1k_1^{(2)}(L-2)f_{L-2} + {}_1k_2^{(2)}(L+2)f_{L+2}] \\
 & + \dots + a_{\ell_0} [{}_{\ell_0}k^0(L)f_{L+\ell_0}{}_{\ell_0}k_1^{(2)}(L-2)f_{L-2} + {}_{\ell_0}k_2^{(2)}(L+2)f_{L+2} \\
 & + \dots + {}_{\ell_0}k_1^{(2\ell_0)}(L-2\ell_0)f_{L-2\ell_0} + {}_{\ell_0}k_2^{(2\ell_0)}(L+2\ell_0)f_{L+2\ell_0}] \\
 & = A \delta_{L1}, \quad \text{and} \tag{II.5}
 \end{aligned}$$

$$f_L = \frac{2L+1}{2L(L+1)} \frac{A}{(c''_0 + a_0)^{-1}} \int \frac{P_L^1(\omega)P_1^1(\omega) d\omega}{1 + \gamma_1 \omega^2 + \gamma_2 \omega^4 + \dots + \gamma_{\ell_0} \omega^{2\ell_0}}. \tag{II.6}$$

We want to show that (II.6) satisfies (II.5). For this purpose we note that from (II.4), (II.6) and (6.32), it follows that

$$\begin{aligned}
 & {}_1k^0(L)f_L + {}_1k_1^{(2)}(L-2)f_{L-2} + {}_1k_2^{(2)}(L+2)f_{L+2} \\
 & = \frac{2L+1}{2L(L+1)} \frac{A}{c''_0 + a_0} \int \frac{\omega^2 P_L^1(\omega)P_1^1(\omega) d\omega}{1 + \gamma_1 \omega^2 + \dots + \gamma_{\ell_0} \omega^{2\ell_0}}, \tag{II.7}
 \end{aligned}$$

$$\begin{aligned}
 & {}_2k^0(L)f_L + {}_2k_1^{(2)}(L-2)f_{L-2} + {}_2k_2^{(2)}(L+2)f_{L+2} \\
 & + {}_4k_1^{(4)}(L-4)f_{L-4} + {}_2k_2^{(4)}(L+4)f_{L+4} \\
 & = \frac{2L+1}{2L(L+1)} \frac{A}{c''_0 + a_0} \int \frac{\omega^4 P_L^1(\omega)P_1^1(\omega) d\omega}{1 + \gamma_1 \omega^2 + \dots + \gamma_{\ell_0} \omega^{2\ell_0}}, \tag{II.8}
 \end{aligned}$$

and so on. On substituting (II.7), (II.8) etc. in (II.5) it is immediately seen that (II.5) is satisfied since

$$\frac{2L+1}{2L(L+1)} \int P_L^1(\omega) P_L^1(\omega) d\omega = \delta_{L1} \quad .$$

Thus, with the help of (II.4) and (6.32), we have shown that (II.6) satisfies (II.5).

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Pseudopotential Form Factors for 11 Alloys

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Explanation of the Tables

The following tables give the form factors for eleven alloys calculated from the Harrison pseudopotential¹. For the impurity ion a proper account has been taken of the change in the surroundings² of the ion compared to the case when it was in the pure metal. Since most applications depend on the relative values of the host and the impurity form factors and since various pseudopotential calculations differ considerably in detail (e.g. in the calculation of the screening, inclusion of the effects of exchange and correlation, inclusion of the influence of the effective mass, and so on) we also give the values of the form factors of the host obtained in a manner similar to the results for the impurity.

The eleven alloys for which the calculations were made are (Mg, Zn, Ca) in Al; (Al, Li) in Mg; (Na, K) in K; (Li, K) in Na. For each host we first give the form factors of the impurities and then for the host. For each ion the first column is the reduced unit q/k_F where k_F is for the host. The next two columns give the screened form factors in rydbergs. The first set of form factors was obtained by setting $m^*/m = 1$; in the other the correction for the influence of effective mass has been applied.

1. Host Al Form Factors of Mg, Zn, Ca, Al.

Magnesium				Zinc			
0.1	-0.35188091E 00	-0.41961789E 00	0.1	-0.35500365E 00	-0.47617084E 00		
0.2	-0.34501219E 00	-0.41121727E 00	0.2	-0.35941482E 00	-0.47738338E 00		
0.3	-0.33309743E 00	-0.39663225E 00	0.3	-0.36298776E 00	-0.47579026E 00		
0.4	-0.31558383E 00	-0.37544394E 00	0.4	-0.36161405E 00	-0.46757299E 00		
0.5	-0.29204679E 00	-0.34741861E 00	0.5	-0.35156381E 00	-0.44937265E 00		
0.6	-0.26250589E 00	-0.31281096E 00	0.6	-0.33071709E 00	-0.41949993E 00		
0.7	-0.22756875E 00	-0.27247971E 00	0.7	-0.29908323E 00	-0.37841785E 00		
0.8	-0.18843669E 00	-0.22786796E 00	0.8	-0.25862569E 00	-0.32350766E 00		
0.9	-0.14674681E 00	-0.18083167E 00	0.9	-0.21246845E 00	-0.27324569E 00		
1.0	-0.10435498E 00	-0.13338786E 00	1.0	-0.16397893E 00	-0.21625412E 00		
1.1	-0.63089728E-01	-0.87480128E-01	1.1	-0.11607385E 00	-0.16060632E 00		
1.2	-0.24571836E-01	-0.44795036E-01	1.2	-0.70832789E-01	-0.10844451E 00		
1.3	0.99027157E-02	-0.66518188E-02	1.3	-0.29477477E-01	-0.60977638E-01		
1.4	0.39410770E-01	0.26035488E-01	1.4	-0.74909925E-02	-0.18646061E-01		
1.5	0.63381135E-01	0.52716017E-01	1.5	0.40107965E-01	0.18679142E-01		
1.6	0.81546068E-01	0.73163092E-01	1.6	0.68776011E-01	0.51528275E-01		
1.7	0.93873203E-01	0.87387681E-01	1.7	0.94225824E-01	0.80759406E-01		
1.8	0.10049021E 00	0.95568001E-01	1.8	0.11745459E 00	0.10751617E 00		
1.9	0.10159481E 00	0.97957015E-01	1.9	0.13965613E 00	0.13315570E 00		
2.0	0.96593440E-01	0.94035506E-01	2.0	0.16076273E 00	0.15781814E 00		

Calcium

Aluminium

0.1	-0.17366982E 00	-0.31586266E 00	0.1	-0.57113701E 00	-0.64493251E 00
0.2	-0.17363739E 00	-0.31180000E 00	0.2	-0.55894530E 00	-0.63081640E 00
0.3	-0.16975212E 00	-0.30137348E 00	0.3	-0.53843480E 00	-0.60719597E 00
0.4	-0.15796852E 00	-0.28087997E 00	0.4	-0.50968009E 00	-0.57430708E 00
0.5	-0.13461494E 00	-0.24708557E 00	0.5	-0.47306174E 00	-0.53273386E 00
0.6	-0.97774506E-01	-0.19861889E 00	0.6	-0.42943704E 00	-0.48358941E 00
0.7	-0.48028946E-01	-0.13665581E 00	0.7	-0.38017237E 00	-0.42849803E 00
0.8	0.11574984E-01	-0.64819336E-01	0.8	-0.32703805E 00	-0.36948824E 00
0.9	0.76288342E-01	0.11632621E-01	0.9	-0.27201182E 00	-0.30874842E 00
1.0	0.14071876E 00	0.86916566E-01	1.0	-0.21705031E 00	-0.24840367E 00
1.1	0.19985735E 00	0.15574408E 00	1.1	-0.16391599E 00	-0.19032252E 00
1.2	0.24975252E 00	0.21400636E 00	1.2	-0.11404967E 00	-0.13600618E 00
1.3	0.28776157E 00	0.25899523E 00	1.3	-0.68531632E-01	-0.86552858E-01
1.4	0.31244308E 00	0.28928077E 00	1.4	-0.28092563E-01	-0.42680800E-01
1.5	0.32326168E 00	0.30438125E 00	1.5	0.68452358E-02	-0.47807693E-02
1.6	0.32021654E 00	0.30438268E 00	1.6	0.36107540E-01	0.27017474E-01
1.7	0.30356115E 00	0.28963274E 00	1.7	0.59708774E-01	0.52775204E-01
1.8	0.27360010E 00	0.26054138E 00	1.8	0.77792346E-01	0.72692692E-01
1.9	0.23058105E 00	0.21746516E 00	1.9	0.90558171E-01	0.87032020E-01
2.0	0.17336845E 00	0.15937883E 00	2.0	0.97338080E-01	0.95210493E-01

2. Host Mg, Form Factors of Al, Li, Mg

Aluminium				Lithium			
0.1	-0.55146450E 00	-0.59956241E 00	0.1	-0.16907400E 00	-0.18924963E 00		
0.2	-0.54347205E 00	-0.59067625E 00	0.2	-0.16707146E 00	-0.18683219E 00		
0.3	-0.52992910E 00	-0.57566941E 00	0.3	-0.16348082E 00	-0.18257314E 00		
0.4	-0.51074600E 00	-0.55451012E 00	0.4	-0.15805149E 00	-0.17626107E 00		
0.5	-0.48594773E 00	-0.52729303E 00	0.5	-0.15051532E 00	-0.16767251E 00		
0.6	-0.45581764E 00	-0.49439478E 00	0.6	-0.14067709E 00	-0.15666032E 00		
0.7	-0.42094404E 00	-0.45650822E 00	0.7	-0.12847394E 00	-0.14320713E 00		
0.8	-0.38222235E 00	-0.41464031E 00	0.8	-0.11400747E 00	-0.127445392E 00		
0.9	-0.34077144E 00	-0.37001270E 00	0.9	-0.97536147E-01	-0.10969228E 00		
1.0	-0.29781151E 00	-0.32393980E 00	1.0	-0.79442203E-01	-0.90327859E-01		
1.1	-0.25454640E 00	-0.27769732E 00	1.1	-0.60176015E-01	-0.69831133E-01		
1.2	-0.21206546E 00	-0.23242605E 00	1.2	-0.40205121E-01	-0.48685014E-01		
1.3	-0.17127752E 00	-0.18906832E 00	1.3	-0.19967675E-01	-0.27339816E-01		
1.4	-0.13289273E 00	-0.14834195E 00	1.4	0.15759468E-03	-0.61841011E-02		
1.5	-0.97416818E-01	-0.11075205E 00	1.5	0.19867480E-01	0.14472961E-01		
1.6	-0.65179646E-01	-0.76611817E-01	1.6	0.38939297E-01	0.34407377E-01		
1.7	-0.36364138E-01	-0.46078920E-01	1.7	0.57229176E-01	0.53479150E-01		
1.8	-0.11040092E-01	-0.19187868E-01	1.8	0.74668705E-01	0.71632326E-01		
1.9	0.10759115E-01	0.40742755E-02	1.9	0.91257393E-01	0.88890910E-01		
2.0	0.27828332E-01	0.22576034E-01	2.0	0.10665917E 00	0.10496557E 00		

Magnesium

0.1	-0.35207403E 00	-0.40339476E 00
0.2	-0.34718639E 00	-0.39747339E 00
0.3	-0.33870608E 00	-0.38731390E 00
0.4	-0.32637280E 00	-0.37273097E 00
0.5	-0.30996835E 00	-0.35358655E 00
0.6	-0.28943676E 00	-0.32994956E 00
0.7	-0.26499617E 00	-0.30215973E 00
0.8	-0.23715967E 00	-0.27085614E 00
0.9	-0.20669252E 00	-0.23692214E 00
1.0	-0.17454332E 00	-0.20140004E 00
1.1	-0.14172965E 00	-0.16538239E 00
1.2	-0.10925227E 00	-0.12991643E 00
1.3	-0.78010201E-01	-0.95926821E-01
1.4	-0.48761845E-01	-0.64177394E-01
1.5	-0.22094309E-01	-0.35245717E-01
1.6	0.15707016E-02	-0.95394254E-02
1.7	0.21959484E-01	0.12694299E-01
1.8	0.38929820E-01	0.31346083E-01
1.9	0.52405238E-01	0.46380460E-01
2.0	0.61307311E-01	0.56785583E-01

3. Host Li. Form Factors of Na, K, Li

Sodium			Potassium		
0.1	-0.22040862E 00	-0.45874584E 00	0.1	-0.15117741E 00	-0.64138794E 00
0.2	-0.21967083E 00	-0.45403469E 00	0.2	-0.15373707E 00	-0.63496876E 00
0.3	-0.21795058E 00	-0.44576937E 00	0.3	-0.15649796E 00	-0.62294102E 00
0.4	-0.21474618E 00	-0.43362963E 00	0.4	-0.15779400E 00	-0.60411453E 00
0.5	-0.20943427E 00	-0.41724569E 00	0.5	-0.15566254E 00	-0.57713604E 00
0.6	-0.20142335E 00	-0.39635992E 00	0.6	-0.14829254E 00	-0.54100990E 00
0.7	-0.19027627E 00	-0.37094218E 00	0.7	-0.13442802E 00	-0.49545002E 00
0.8	-0.17579758E 00	-0.34125018E 00	0.8	-0.11365265E 00	-0.44112206E 00
0.9	-0.15808880E 00	-0.30785078E 00	0.9	-0.86502552E-01	-0.37966031E 00
1.0	-0.13754386E 00	-0.27158070E 00	1.0	-0.54424882E-01	-0.31355864E 00
1.1	-0.11480486E 00	-0.23346913E 00	1.1	-0.19537091E-01	-0.24582577E 00
1.2	-0.90681434E-01	-0.19463533E 00	1.2	0.15685618E-01	-0.17966497E 00
1.3	-0.66058815E-01	-0.15618938E 00	1.3	0.48744678E-01	-0.11809516E 00
1.4	-0.41812420E-01	-0.11914599E 00	1.4	0.77365696E-01	-0.63713014E-01
1.5	-0.18741906E-01	-0.84370375E-01	1.5	0.99698246E-01	-0.18530011E-01
1.6	0.24787784E-02	-0.52536309E-01	1.6	0.11438000E 00	0.16077399E-01
1.7	0.21320760E-01	-0.24118066E-01	1.7	0.12052757E 00	0.39324403E-01
1.8	0.37398994E-01	0.60921907E-03	1.8	0.11764216E 00	0.50902367E-01
1.9	0.50407112E-01	0.21525979E-01	1.9	0.10539424E 00	0.50785363E-01
2.0	0.58529973E-01	0.37114739E-01	2.0	0.80883384E-01	0.36484659E-01

Lithium

0.1	-0.23308414E 00	-0.33217579E 00
0.2	-0.23090893E 00	-0.32849950E 00
0.3	-0.22707510E 00	-0.32218188E 00
0.4	-0.22139937E 00	-0.31309766E 00
0.5	-0.21366423E 00	-0.30111337E 00
0.6	-0.20369351E 00	-0.28616482E 00
0.7	-0.19140118E 00	-0.26830697E 00
0.8	-0.17682052E 00	-0.24773377E 00
0.9	-0.16011256E 00	-0.22477758E 00
1.0	-0.14155209E 00	-0.19987595E 00
1.1	-0.12149465E 00	-0.17353082E 00
1.2	-0.10033983E 00	-0.14626110E 00
1.3	-0.78491926E-01	-0.11855930E 00
1.4	-0.56328833E-01	-0.90858400E-01
1.5	-0.34182191E-01	-0.63516438E-01
1.6	-0.12322009E-01	-0.36800563E-01
1.7	0.90468526E-02	-0.10887623E-01
1.8	0.29788435E-01	0.14145195E-01
1.9	0.49814533E-01	0.38319767E-01
2.0	0.68309069E-01	0.61024066E-01

4. Host Na. Form Factors of Li, K, Na

Lithium			Potassium		
0.1	-0.16419655E 00	-0.18305039E 00	0.1	-0.12695092E 00	-0.21949100E 00
0.2	-0.16305047E 00	-0.18167263E 00	0.2	-0.12753791E 00	-0.21871191E 00
0.3	-0.16103804E 00	-0.17927396E 00	0.3	-0.12799311E 00	-0.21690077E 00
0.4	-0.15806109E 00	-0.17576355E 00	0.4	-0.12777013E 00	-0.21356761E 00
0.5	-0.15400130E 00	-0.17103207E 00	0.5	-0.12616593E 00	-0.20808166E 00
0.6	-0.14875287E 00	-0.16498709E 00	0.6	-0.12246746E 00	-0.19982624E 00
0.7	-0.14224654E 00	-0.15757620E 00	0.7	-0.11608106E 00	-0.18832940E 00
0.8	-0.13446426E 00	-0.14880282E 00	0.8	-0.10662144E 00	-0.17334497E 00
0.9	-0.12545246E 00	-0.13873720E 00	0.9	-0.94014108E-01	-0.15495235E 00
1.0	-0.11531663E 00	-0.12750870E 00	1.0	-0.78517139E-01	-0.13356382E 00
1.1	-0.10421187E 00	-0.11529660E 00	1.1	-0.60698330E-01	-0.10989028E 00
1.2	-0.92326403E-01	-0.10230994E 00	1.2	-0.41381240E-01	-0.84881306E-01
1.3	-0.79864025E-01	-0.88769734E-01	1.3	-0.21541536E-01	-0.59613466E-01
1.4	-0.67027867E-01	-0.74891746E-01	1.4	-0.22079945E-02	-0.35189986E-01
1.5	-0.54004848E-01	-0.60871184E-01	1.5	0.15614510E-01	-0.12663782E-01
1.6	-0.40958583E-01	-0.46874523E-01	1.6	0.31040847E-01	0.70589185E-02
1.7	-0.28023146E-01	-0.33033729E-01	1.7	0.43326259E-01	0.23233652E-01
1.8	-0.15304111E-01	-0.19445769E-01	1.8	0.51893353E-01	0.35307646E-01
1.9	-0.29041730E-02	-0.61933808E-02	1.9	0.56224585E-01	0.42819679E-01
2.0	0.83543286E-02	0.59379973E-02	2.0	0.53635895E-01	0.43175161E-01

Sodium

0.1	-0.15872383E 00	-0.20188642E 00
0.2	-0.15827584E 00	-0.20085829E 00
0.3	-0.15732604E 00	-0.19894707E 00
0.4	-0.15567732E 00	-0.19597495E 00
0.5	-0.15307087E 00	-0.19171029E 00
0.6	-0.14924401E 00	-0.18592787E 00
0.7	-0.14396858E 00	-0.17844647E 00
0.8	-0.13709325E 00	-0.16917270E 00
0.9	-0.12856966E 00	-0.15811855E 00
1.0	-0.11846334E 00	-0.14541399E 00
1.1	-0.10694933E 00	-0.13129258E 00
1.2	-0.94292164E-01	-0.11607158E 00
1.3	-0.80823362E-01	-0.10012496E 00
1.4	-0.66905320E-01	-0.83846807E-01
1.5	-0.52905738E-01	-0.67624629E-01
1.6	-0.39172292E-01	-0.51815033E-01
1.7	-0.26018083E-01	-0.36728799E-01
1.8	-0.13716638E-01	-0.22624731E-01
1.9	-0.25526285E-02	-0.97546577E-02
2.0	0.58302879E-02	0.29474497E-03

5. Host K. Form Factors of Li, Na, K

Lithium				Sodium			
0.1	-0.11633360E 00	-0.10277057E 00	0.1	-0.11451334E 00	-0.85101545E-01		
0.2	-0.11577499E 00	-0.10234487E 00	0.2	-0.11423683E 00	-0.85137188E-01		
0.3	-0.11478901E 00	-0.10158104E 00	0.3	-0.11369044E 00	-0.85111439E-01		
0.4	-0.11332560E 00	-0.10042661E 00	0.4	-0.11280102E 00	-0.84943116E-01		
0.5	-0.11131912E 00	-0.98812461E-01	0.5	-0.11146206E 00	-0.84517300E-01		
0.6	-0.10870546E 00	-0.96669793E-01	0.6	-0.10956490E 00	-0.83710492E-01		
0.7	-0.10543257E 00	-0.93939245E-01	0.7	-0.10700428E 00	-0.82399487E-01		
0.8	-0.10147077E 00	-0.90581954E-01	0.8	-0.10370129E 00	-0.80481221E-01		
0.9	-0.96818745E-01	-0.86585522E-01	0.9	-0.99607587E-01	-0.77880323E-01		
1.0	-0.91505826E-01	-0.81966817E-01	1.0	-0.94717085E-01	-0.74559450E-01		
1.1	-0.85589588E-01	-0.76770723E-01	1.1	-0.89066327E-01	-0.70524752E-01		
1.2	-0.79151869E-01	-0.71066618E-01	1.2	-0.82730353E-01	-0.65821350E-01		
1.3	-0.72288752E-01	-0.64939260E-01	1.3	-0.75818479E-01	-0.60532212E-01		
1.4	-0.65105081E-01	-0.58484223E-01	1.4	-0.68462312E-01	-0.54766655E-01		
1.5	-0.57705227E-01	-0.51799044E-01	1.5	-0.60807168E-01	-0.48653722E-01		
1.6	-0.50187986E-01	-0.44978559E-01	1.6	-0.53002834E-01	-0.42332947E-01		
1.7	-0.42643387E-01	-0.38112499E-01	1.7	-0.45197427E-01	-0.35949886E-01		
1.8	-0.35154600E-01	-0.31288739E-01	1.8	-0.37541151E-01	-0.29661331E-01		
1.9	-0.27829416E-01	-0.24628520E-01	1.9	-0.30234955E-01	-0.23690287E-01		
2.0	-0.21466773E-01	-0.18955573E-01	2.0	-0.24671897E-01	-0.19468222E-01		

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